TABLE IV
REACTIONS OF PENTABORANE(11) AND OF DIMETHYLAMINODIFLUOROPHOSPHINE–TETRABORANE(8) WITH DIMETHYLAMINODIFLUOROPHOSPHINE

Reactant ratio base/B_5H_{11}	Reaction time,[a] hr	% reaction of B_4H_8L[b]	% borane deficiency[c]
3.55	1	0	. . .
4.37	26	78	14
4.55	44	100	13
base/B_4H_8L			
2.55	2	44	7
3.76	8	67	10

[a] At 23°. [b] Per cent of B_4H_8L reacting to produce BH_3L and solid material. [c] Per cent of borane adduct not recovered, assuming 1 mol of borane adduct was produced per mole of tetraborane(8) adduct consumed.

the remaining material became dark yellow. The mass spectrum of the solid, refined and observed at 0°, showed the presence of the diborane(4) and hexaborane(10) adducts.

Dimethylaminodifluorophosphine (3.70 mmol) was used to treat $PF_2N(CH_3)_2B_4H_8$ (0.98 mmol) for 8 hr at 23°. Products were removed at 0° for 65 hr. $PF_2N(CH_3)_2B_4H_8$ (0.33 mmol) and $PF_2N(CH_3)_2BH_3$ (0.56 mmol) were found, and some free base (2.86 mmol) was recovered. The solid that remained gave the same mass spectrum as the one obtained from the solid adduct with pentaborane(9) except that the envelope attributed to pentaborane(9) was absent. At 23° $[PF_2N(CH_3)_2]_2B_2H_4$ was obtained, mp 43°.[5]

Pentaborane(11) with Difluorophosphine.—B_5H_{11} (1.295 mmol) reacted with the PF_2H (4.97 mmol) for 10 min at 23° to produce $PF_2HB_4H_8$ (1.23 mmol, 95% yield)[23] and PF_2HBH_3 (1.290 mmol).

$PF_2HB_4H_8$ (0.994 mmol) reacted with PF_2H (2.54 mmol) for 40 min at 23° to produce PF_2HBH_3 (0.384 mmol),[24] $(PF_2H)_2B_2H_4$ (0.102 mmol),[6] and a yellow solid. Some difluorophosphine–tetraborane(8) was recovered (0.558 mmol). In all of the reactions extensive decomposition of the base prevented a determination of the amount consumed. The difluorophosphine–borane recovered from the reaction between the tetraborane(8) adduct and the base corresponded to 1 mol of borane adduct per mole of tetraborane(8) adduct consumed.

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[24] R. W. Rudolph and R. W. Parry, J. Amer. Chem. Soc., **89**, 1621 (1967).

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Ternary Nitrides of Calcium and Strontium with Molybdenum and Tungsten

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Ternary nitrides of molybdenum and tungsten with the alkaline earth metals calcium and strontium were formed by heating the transition metals with the alkaline earth nitrides in oxygen-free, dry nitrogen at atmospheric pressure. A hexagonal phase (a = 11.40 ± 0.01 Å, c = 7.45 ± 0.01 Å) has been assigned the tentative formula Ca_5MoN_5. A cubic phase is obtained in the Sr–Mo–N system at 750° which is isostructural with $Sr_{27}Re_5N_{28}$. Tungsten yields analogous compounds. At higher temperatures, the strontium compounds form other unidentified phases. Ca_5MoN_5 is an insulator with a temperature-independent paramagnetism similar to $Sr_{27}Re_5N_{28}$. $Sr_{27}W_5N_{28}$ and presumably $Sr_{27}Mo_5N_{28}$ are diamagnetic.

Introduction

The transition metals rhenium and osmium have been shown to yield ternary nitride phases when the metals are heated with strontium and barium nitrides in an atmosphere of nitrogen.[1] It was observed that molybdenum and tungsten also gave rise to new phases when treated in a similar manner. The pelleted mixtures of alkaline earth nitride and molybdenum crumbled to a fine yellow powder with phenomenal increase in bulk during the reaction. The product appeared to be a mixture which could not be resolved. In the present investigation it was found that this peculiar behavior was due to the inadvertent presence of small amounts of moisture or oxygen in the system. When suitable precautions were taken to eliminate these, ternary nitrides were obtained. This paper reports the preparation and some of the properties of the compounds obtained with molybdenum and tungsten.

There is a special interest in the fixation of nitrogen by molybdenum in view of the significant role played by molybdenum complexes in biological systems. The compounds described here are extremely reactive in protonic solvents, but no derivative chemistry has yet been developed.

Experimental Section

Materials.—The molybdenum and tungsten metals (200 mesh) were obtained from Alfa Inorganics Inc. The purity of each was 99.7% (99.9% based on metallic content only). Before use, these metals were heated at 900° in a stream of Extra Dry grade hydrogen for about 3 hr to remove any surface oxide. Pure nitrogen was obtained by decomposition of sodium azide by cautious heating in an evacuated round-bottomed flask directly attached to the vacuum line. The sodium produced in the reaction $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$ appears as a fine dispersion and serves as a useful getter for moisture and oxygen.

Calcium metal 99.9% pure with respect to other metals contains appreciable portions of oxide. It was distilled twice at 900° and 10^{-6} mm in a stainless steel container. The distilled metal collected on a metal plug at the cooler end of the container which was heated by induction. Strontium metal (98–99%) was similarly treated. The binary nitrides Ca_3N_2 and Sr_3N_2 were prepared by heating the distilled metals in 1 atm of nitrogen at 750° for several days.

The handling of all air- and moisture-sensitive materials was

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[1] F. K. Patterson and R. Ward, Inorg. Chem., **5**, 1312 (1966).

carried out in glove bags filled with dry nitrogen. The metal powders and the alkaline earth nitrides were intimately mixed in a Spex-500 mixer using an agate vial with an agate grinding ball. Samples were presssed into pellet form and placed in a molybdenum boat in the silica heating chamber. This was attached to the vacuum line and pumped down to 10^{-6} mm before the pure nitrogen was introduced.

For reasons not determined, it was found necessary to resort to a tedious heating process usually requiring at least 1 week for complete reaction as indicated by the attainment of constant pressure in the system. The mixtures were preheated at 450° for 1 day although no appreciable absorption of nitrogen occurred below 700°. Subsequent treatment was in general 1 day each at 750, 820, 860, and 950°. More prolonged heating at 820° seemed to give more crystalline products. The X-ray powder diffraction patterns were obtained with a General Electric XRD-5 diffractometer using Ni-filtered Cu Kα radiation (λ 1.542 Å) and a proportional counter. The samples were prepared for measurement as previously described.[1]

(1) **Calcium Molybdenum Nitride.**—Variation of the Ca/Mo ratio in the mixtures gave products which showed by X-ray analysis the presence of calcium nitride in preparations where the ratio was greater than 5 and the presence of β-molybdenum nitride and molybdenum metal where the ratio was less than 5.

The valence of the molybdenum in the compound was estimated by measuring the uptake of nitrogen by mixtures having a Ca/Mo ratio greater than 5. Samples containing 2.962×10^{-3} and 3.705×10^{-3} g-atom of molybdenum absorbed 2.55×10^{-3} and 3.13×10^{-3} mol of N_2, respectively. In this way, a molybdenum valence of 5.12 ± 0.06 was obtained.

The product is a brown powder giving the X-ray diffraction pattern listed in Table I which can be indexed on the basis of a hexagonal unit cell $a = 11.40 \pm 0.01$ Å, $c = 7.45 \pm 0.01$ Å. The density measured by CCl_4 displacement is 2.90 g/cm^3 which corresponds to four Ca_5MoN_5 formula units per unit cell (2.89 g/cm^3).

TABLE I

OBSERVED AND CALCULATED *d* VALUES FOR HEXAGONAL CALCIUM MOLYBDENUM NITRIDE ($a = 11.40 \pm 0.01$ Å, $c = 7.45 \pm 0.01$ Å)

hkl	*d*(obsd), Å	*d*(calcd), Å	*I*
220	2.847	2.847	95.95
221	2.650	2.660	Very weak[a]
311	2.562	2.567	Very weak[a]
400	2.466	2.466	100
204	1.742	1.742	35.2
404	1.487	1.486	13.3
205	1.426	1.426	5.1
443	1.235	1.235	Very weak[a]
640	1.132	1.131	1.6
624	1.103	1.102	1.6
625	1.007	1.007	1.8

[a] Too weak to measure accurately.

It was not found possible to remove excess calcium nitride from the products by selective solvolysis in liquid ammonia–ammonium nitrate solutions or by thermal decomposition, procedures which were found useful in the synthesis of $Ba_9Re_3N_{10}$.[1] Consequently, chemical analysis of the products is of limited value. *Anal.* Calcd for Ca_5MoN_5: Ca, 54.7; Mo, 26.2; N, 19.1. Found: Ca, 53.6 ± 0.2; Mo, 25.3 ± 0.3; N, 18.8 ± 0.2. The nitrogen was determined by the Kjeldahl method, the molybdenum by X-ray fluorescence, and the calcium by titration with EDTA.

A qualitative test using a Simpson volt-ohm-ammeter on a pelleted sample suggests that the compound is an insulator at room temperature. It has an essentially temperature-independent paramagnetism from 77 to 285°K. About 30 readings were taken over this temperature range. The sample contained a ferromagnetic impurity presumably introduced from the iron vessel used in the distillation of the calcium metal. After correction for this, the value of χ_M found was 900×10^{-6} cgsu at room temperature and 910×10^{-6} cgsu at 77°K. Assuming zero Weiss constant, this corresponds to $\mu_{eff} = 1.46$ BM at room temperature.

Calcium molybdenum nitride is an extremely reactive substance. A small amount placed in 10 ml of water gives a violent reaction. The nitride particles glow red, and a vigorous evolution of gas ensues. The gas often ignites spontaneously. It contains ammonia and presumably hydrogen. The white residue which remains is a mixture of calcium hydroxide and calcium molybdate. The reaction may be represented by the equation $24H_2O + 2Ca_5MoN_5 \rightarrow 8Ca(OH)_2 + 2CaMoO_4 + 10NH_3 + H_2$. A similar kind of reaction occurs with aqueous acids, but butyric acid gave no reaction. No reaction occurred with boiling phenols or alcohols. Calcium molybdenum nitride neither reacts with nor dissolves in liquid ammonia. However, it readily dissolves in a liquid ammonia–ammonium nitrate solution. The thermal stability of this compound was not extensively studied, but, in 1 atm of nitrogen, calcium molybdenum nitride appears to be stable at 1000°.

(2) **Calcium Tungsten Nitride.**—The reaction of tungsten with calcium nitride proceeds in much the same manner as that of molybdenum. After preheating the mixtures at 450° for 1 day, the temperature was raised to 750°, the temperature at which nitrogen absorption occurs. Subsequent heating at 800° for 1 week completed the reaction. The reactions were slower than those with molybdenum, and products completely free from tungsten metal were not obtained. The only compound formed is apparently isotypic with the ternary molybdenum compound and was assumed to have a formula close to Ca_5WN_5. No binary nitride of tungsten was formed in the reactions of any of the mixtures. The X-ray pattern of the tungsten compound is given in Table II. Lines corresponding to the weak reflections of the molybdenum compound did not appear, but the stronger lines have almost the same *d* values. The density of the purest product was 3.86 g/cm^3 which is higher than the theoretical (3.60 g/cm^3) presumably because of the presence of tungsten metal.

TABLE II

OBSERVED AND CALCULATED *d* VALUES FOR HEXAGONAL CALCIUM TUNGSTEN NITRIDE

hkl[a]	*d*(obsd), Å	*d*(calcd), Å	*I*
220	2.849	2.847	100
221	2.666	2.660	Very weak
400	2.466	2.466	86.8
204	1.743	1.742	28.4
404	1.486	1.486	9.2
205	1.426	1.426	5.5

[a] The *hkl* values given here are assuming the presence of the unobserved ordering line found for Ca_5MoN_5.

The magnetic behavior of calcium tungsten nitride parallels that of the molybdenum compound, $\chi_M = 700 \times 10^{-6}$ cgsu at room temperature and 780×10^{-6} cgsu at liquid nitrogen temperature; μ_{eff} at room temperature assuming zero Weiss constant is 1.34 BM. The chemical reactivity of the compound is similar to that of Ca_5MoN_5.

(3) **Strontium Molybdenum Nitrides.**—The same procedures were followed for this system as for the calcium molybdenum nitride. By variation of the composition of the mixtures and by varying the temperatures, it was found that a ternary compound was formed below 750° which was isomorphous with cubic $Sr_{27}Re_5N_{28}$.[1] A mixture of strontium nitride and molybdenum powder in which Sr/Mo = 5.5 heated at 450° for 1 day and for 1 week at 750° gave a brown product. The diffraction pattern (Table III) corresponded closely to that of $Sr_{27}Re_5N_{28}$—the lattice parameters of both compounds being virtually identical ($a = 5.25 \pm 0.01$ Å). On this basis we assume that the formula is $Sr_{27}Mo_5N_{28}$. Due to the slowness of the reaction, the product was always contaminated with the reactants. At 800–850° there is conversion to a white product and at 950° to a yellow powder.

TABLE III

DIFFRACTION PATTERNS OF $Sr_{27}M_5N_{28}$
(a = 5.25 ± 0.01 Å)

hkl for $Sr_{27}M_5$-N_{28}[a]	d(obsd) for $Sr_{27}Mo_5N_{28}$, Å	I(obsd) for $Sr_{27}Mo_5N_{28}$	d(obsd) for $Sr_{27}W_5N_{28}$, Å	I(obsd) for $Sr_{27}W_5N_{28}$	d(calcd) for $Sr_{27}M_5N_{28}$, Å
111	3.014	100	3.025	100	3.028
200	2.626	44.0	2.631	43.0	2.622
220	1.854	18.1	1.857	19.4	1.855
311	1.581	9.3	1.583	10.3	1.582
222	1.515	5.2	1.518	4.9	1.517

[a] M = Mo or W.

The complex diffraction patterns of these phases were not resolved. The structures are not apparently related to that of $Sr_9Re_3N_{10}$ which is formed by the decomposition of $Sr_{27}Re_5N_{28}$. Since none of the compounds was obtained pure, the properties were not determined. They are all highly reactive with water and acids.

(4) **Strontium Tungsten Nitrides.**—The Sr–W–N system appears to be strictly analogous to the molybdenum system. An isotypic brown cubic phase was formed at 800° and is assumed to have the formula $Sr_{27}W_5N_{28}$. It is diamagnetic at room temperature. The *d*-spacing values of the product are identical with those of the analogous molybdenum compound. They are listed in Table III. Other phases with complex X-ray diffraction patterns are formed upon heating this compound at 850 and 950° in nitrogen but these phases were not characterized.

Discussion

The major difference between the ternary nitrides of molybdenum and tungsten and those of rhenium from the experimental side is the extreme sensitivity of the former to the presence of oxygen during synthesis. Attempts to determine by monitored additions the amount of oxygen which could be tolerated were not successful. The compositions of the oxynitride phases could not be estimated by this procedure.

The formula for the calcium molybdenum nitride Ca_5MoN_5 must be regarded as tentative in view of our inability to solve the structure from X-ray powder diffraction data and due to the difficulty of obtaining samples, the purity of which could be established beyond question. We were not able to obtain single crystals. The magnetic data suggest that the nitride relates in some ways to $Sr_{27}Re_5N_{28}$. The transition metal in each case would have one d electron. The large hexagonal cell containing $Ca_{20}Mo_4N_{20}$ allows the possibility that the structure is based on the lattice of a 1:1 compound with four anion sites vacant, the cation sites being fully occupied by calcium and molybdenum ions in a random fashion. It is possible that each molybdenum could be associated with a nitrogen vacancy. These are essentially the features proposed for $Sr_{27}Re_5N_{28}$ which, however, contains one unique rhenium.

The effective moments calculated for molybdenum (1.46 BM) and tungsten (1.30 BM) are higher than the moments which are expected for d^1 cations with high spin–orbit coupling constants in a field of perfect cubic symmetry. At room temperature, the theoretical moment for Mo^{5+} is approximately 0.90 BM, and for W^{5+} it is about 0.75 BM. These values would increase as the field becomes distorted.[2] The experimental values might then be reasonable with a hexagonal structure having the feature proposed—especially the association of the M^{5+} ion with a nitrogen vacancy. The experimental values of the moments reported here must, however, be considered tentative since they are calculated on the assumption of a zero Weiss constant. Nonetheless, it is unlikely that the assumption would produce sizable errors. In this respect, it is interesting to note that quinquevalent molybdenum and tungsten ions frequently give rise to moments substantially greater than those derived from a theory which ingores distortion effects.[3]

The chemical analysis reveals a significant impurity in the sample. The sum of the percentages is only 97.5%. This might be attributable to the high reactivity of the compound with moisture which could be quite extensive because the products are so finely divided. If such a reaction were to follow the hydrolysis equation, one would expect the impurity to consist entirely of hydrogen (as the hydroxide) and oxygen. The analysis of a sample containing a 2.5% impurity should give 53.8% Ca, 25.8% Mo, 17.9% N, 2.4% O, and 0.1% H. The experimental results are in reasonably good agreement with these values.

The conclusion that the compound is stoichiometric is based upon the constancy of the X-ray diffraction data from products of mixtures with different Ca/Mo starting ratios. The necessity for the large unit cell depends on one faint but constantly recurring reflection which could not be attributed to likely impurities. The formula may differ slightly from the one proposed. $Ca_{19}Mo_4N_{20}$ (containing 5.5% Mo) would correspond to the analytical data, for example. This uncertainty can only be resolved by single-crystal X-ray analysis. Attempts to grow single crystals from calcium chloride fluxes were not successful.

The preparation of molybdenum and tungsten phases analogous to $Sr_{27}Re_5N_{28}$ is interesting inasmuch as it represents the first ternary nitrides involving the alkaline earth cations in which the transition metal has its maximum oxidation state. The diamagnetism of the tungsten compound confirms this. In the ternary nitrides of lithium with transition metals, Juza and his coworkers[2-8] found that the antifluorite structure was most frequently observed with the cations occupying the tetrahedral sites. The transition metals are in their highest oxidation states. A structure of high lattice energy—one based on the close-packing of ions—is probably the most important factor in stabilizing these compounds. The $Sr_{27}M_5N_{28}$ compounds could owe their existence to the close-packed nature of the structure (NaCl type). The thermal decomposition of the rhenium compound, however,

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leads to a black nitride in which the rhenium is tetravalent[1] whereas heating the molybdenum and tungsten compounds above their preparation temperatures gives white products—most likely containing Mo(6) and W(6).

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The Tetrafluorobromate(III) Anion, BrF_4^-

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The NO^+, NO_2^+, K^+, and Cs^+ salts of BrF_4^- have been prepared and characterized. It is shown by vibrational spectroscopy that the BrF_4^- anion is planar and not tetrahedral. The structure and bonding of BrF_4^- is similar to that of the ClF_4^- anion.

Introduction

Bromine trifluoride possesses amphoteric character and forms adducts with strong Lewis bases.[1] Thus, the existence of the salts $K^+BrF_4^-$,[2] $Rb^+BrF_4^-$,[3a] and $NO^+BrF_4^-$ [3b] has previously been reported. Only one attempt was made to establish the structure of the BrF_4^- anion. Siegel reported[4] the X-ray powder pattern of $K^+BrF_4^-$ and concluded on the basis of intensity calculations that BrF_4^- is tetrahedral. Later, Sly and Marsh pointed out[5] that Siegel's data might equally well be interpreted in terms of a square-planar configuration. No further data on the structure of BrF_4^- have been reported, thus leaving the problem unresolved.[6] In the course of a systematic investigation of adducts derived from bromine fluorides, we have also studied a number of BrF_4^--containing salts. In this paper we wish to report the data obtained for $NO^+BrF_4^-$, $K^+BrF_4^-$, $Cs^+BrF_4^-$, and $NO_2^+BrF_4^-$. The preparation of $Cs^+BrF_4^-$ has previously not been reported. Aynsley and coworkers[7] believed they had prepared material containing $NO_2^+BrF_4^-$; however, they did not successfully isolate or characterize the adduct.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise, Bourdon tube-type gauge (0–1500 mm ± 0.1%). Bromine trifluoride (from the Matheson Co.) was purified by fractional condensation, the material retained at −23° being used. It was nearly white as a solid and pale yellow as a liquid. Nitryl fluoride and nitrosyl fluoride (prepared from F_2 and N_2O_4 and NO, respectively) were purified by fractional condensation. The alkali metal fluorides were fused in a platinum crucible and powdered in a drybox prior to use. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Because of their hygroscopicity, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

For the dissociation pressure measurements the $NO_2F \cdot BrF_3$ complex was prepared in a Teflon FEP U trap directly connected to a Heise gauge. Pressures were read to the nearest millimeter and the temperature of the cooling bath was determined with a copper–constantan thermocouple. Equilibrium pressures were approached from above and below a given temperature. Equilibrium was assumed when the pressure was constant at a given temperature for at least 30 min. The following temperature (°K)–vapor pressure (mm) data were observed: increasing temperature: 259.5, 12; 266.8, 20; 273.2, 35; 278.3, 51; 282.8, 71; 289.8, 121; 294.8, 176; decreasing temperature: 292.9, 163; 283.0, 75; 273.2, 36. The best fit of log P *vs.* T^{-1} was obtained by the method of least squares.

Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper $K\alpha$ radiation and a nickel filter. Samples were sealed in Lindemann glass tubes (∼0.3- and ∼0.5-mm o.d.).

The infrared spectra were recorded on a Beckman Model IR-7 with CsI interchange and Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The low-temperature spectra were taken by preparing the complex on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex glass, all windows being AgCl. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP

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