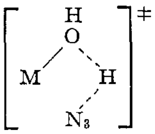
For the reasons cited by Sutin and coworkers[7] the anation reaction of V^{3+} with SCN^- has considerably more S_N2 character than, for example, the corresponding reactions of Fe^{3+} and $(NH_3)_5CoH_2O^{3+}$. In the latter cases[2,3,5,6,10,11,23] the predominant rate-determining feature is the dissociation of a coordinated water molecule from the ion pair M^{3+},NCS^-. Cr(III) appears to follow a mechanism[4] intermediate in character between that ascribed to V(III), on the one hand, and to Fe(III) and Co(III), on the other. In view of the mechanistic differences, the very low value of 0.004 for the ratio k_{HN_3}/k_{NCS} for V^{3+} is not surprising since a ligand dependence is expected for an S_N2 process.

The rate term $d[L_5MOH_2{}^{3+}][HN_3]/[H^+]$, or its equivalent $k_3[L_5MOH^{2+}][HN_3]$, provides an important pathway for all four M(III)'s listed in Table IV, whereas the term $k_3'[L_5MOH^{2+}][NCS^-]$ contributes appreciably only for Fe^{3+} and Cr^{3+} and not for V^{3+} [25] and $(NH_3)_5Co^{3+}$. The origin of the second term arises from the π-bonding effect of OH^- in dissociative mechanisms where the OH^- is retained in the primary product as with Fe(III) and Cr(III). In $(NH_3)_5CoOH^{2+}$, on the other hand, OH^- is not retained, but rather it is the leaving group. The effect of OH^- would be far less if bond breaking is not the main rate-controlling aspect, as appears to be the case with V^{3+}. The reactivity of MOH^{2+} toward HN_3 (or of M^{3+} toward N_3^-) in all cases supports Swaddle and Guastalla's contention[5] that a specific effect is present in the azide case, which may be the hydrogen bonding of azide ion



The second-order rate constant k_1 for the reaction of $V(H_2O)_6{}^{3+}$ and N_3^-, were Scheme I and not Scheme II responsible for the rate term $d[V^{3+}][HN_3]/[H^+]$, can be computed from the value of d and the acid dissociation constant of HN_3. The latter value[26] is $Q_a = 7 \times 10^{-5}\ M$, giving $k_1 = 9 \times 10^2\ M^{-1}\ sec^{-1}$. This is a value somewhat higher than that for SCN^- (114 $M^{-1}\ sec^{-1}$) or for oxalic acid[27] ($6.9 \times 10^2\ M^{-1}\ sec^{-1}$). Because bond making predominates, it is not possible to state the k_1 value is unreasonably high on that basis alone, although the other lines of evidence strongly suggest Scheme II is the correct mechanism.

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(25) Sutin, *et al.*,[7] gave an upper limit of 0.03 sec^{-1} for the value of k in the term $k[V^{3+}][SCN^-]/[H^+]$ which leads to the value $\leq 22\ M^{-1}\ sec^{-1}$ for the second-order rate constant for $VOH^{2+} + NCS^-$ using $K_h = 1.4 \times 10^{-3}$ for V^{3+}: L. Pajdowski, *J. Inorg. Nucl. Chem.*, **28**, 443 (1966). From the results obtained here the value of k_3 for $VOH^{2+} + HN_3$ in Scheme II is 44 $M^{-1}\ sec^{-1}$ ($k_3 = k/K_h$).

(26) M. Quintin, *Compt. Rend.*, **210**, 625 (1940).

(27) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968). In this reaction the dependence on $[H^+]$ apparently was not examined, so resolution of this rate constant into true second-order rate constants is not possible.

Contribution from the Chemistry Department,
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The Preparation of β-Molybdenum Nitride

By RONALD KARAM and ROLAND WARD

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The preparation of pure β-molybdenum nitride, stable at room temperature, is achieved by reaction of the elements catalyzed by calcium nitride. The X-ray powder diffraction pattern is indexed using a tetragonal unit cell, $a = 8.41$ Å and $c = 8.05$ Å. The suggested formula is $Mo_{16}N_7$. The compound has a temperature-independent paramagnetism above 175°K. Below this temperature, Curie–Weiss behavior is observed.

In the investigation of the system Ca–Mo–N[1] it was found that the mixtures with Ca:Mo ratios less than 5 gave rise to a phase other than hexagonal Ca_5MoN_5. The new phase was first thought to be a second ternary nitride. The diffraction pattern was later identified as that of β-molybdenum nitride which had been characterized by Hägg[2] as a metastable molybdenum nitride formed in the reaction between molybdenum and ammonia at temperatures above 600°. It was always contaminated with the α-molybdenum phase and Mo_2N in samples obtained by quenching from temperatures above 600°. The phase was identified by the presence in the X-ray powder diffraction pattern of reflections which could be indexed on the basis of a tetragonal unit cell with $a = 4.180$ Å and $c = 4.016$ Å. It was estimated to contain 28 atom % nitrogen.

The products we obtained by reactions occurring at 750° and with slow cooling were uncontaminated by either α-molybdenum or Mo_2N. This paper describes the preparations and properties of pure β-molybdenum nitride.

Experimental Section

The materials and general procedures are similar to those to be described.[1] The heat treatment of the intimate mixtures of calcium nitride and molybdenum which gave the best results involved heating for 1 day at 450° and for 2 weeks at 750°. The pressure of nitrogen was maintained at about 1 atm. The mix-

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(1) R. Karam and R. Ward, to be submitted for publication.

(2) G. Hägg, *Z. Physik. Chem.*, **7**, 339 (1930).

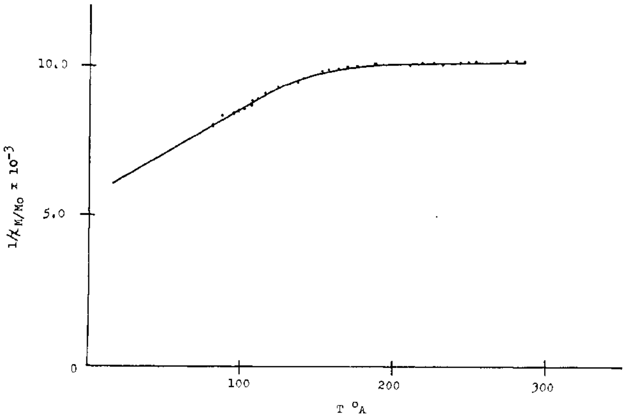

Figure 1.—Plot of $1/\chi_M$ *vs.* temperature for $Mo_{16}N_7$.

tures may contain as little as 1 mol % of calcium nitride to obtain complete conversion of the molybdenum to β-molybdenum nitride. With less than this proportion, the reaction is much slower. Only a trace of the β phase could be found in pure molybdenum subjected to the same treatment.

The products of these reactions were treated several times with cold 6 *N* hydrochloric acid to remove any calcium compound. The product is a brittle material and rather inert chemically. It resembles the hard nitrides in properties. The composition was determined by measuring the nitrogen absorption gravimetrically and volumetrically. The solution obtained by dissolving the nitride in aqua regia contained no detectable calcium. Molybdenum was not directly determined. The samples analyzed contained no molybdenum detectable by X-ray analysis.

The amount of nitrogen found was 6.07% or about 30.6 atom %. The closest rational formula is $Mo_{16}N_7$. Strontium nitride was also effective in the preparation of the β-molybdenum nitride but less so than calcium nitride.

The X-ray diffraction pattern is given in Table I. It can be satisfactorally indexed on the basis of a tetragonal cell with a = 8.41 Å and c = 8.05 Å. The large unit cell is required by the presence of several superlattice lines. The density measured by displacement of CCl_4 was found to be 9.3 g/cm³. The calculated density assuming two $Mo_{16}N_7$ units per unit cell is 9.5 g/cm³.

Table I

Diffraction Pattern of β-Molybdenum Nitride

d, Å			
Obsd	Calcd	*hkl*	*I*
2.396	2.390	222	100
2.262	2.260	203	2
2.106	2.109	400	48
2.012	2.010	004	15
1.538	1.539	423	1
1.487	1.486	440	15
1.453	1.452	404	27
1.261	1.262	622	35
1.221	1.221	226	8
1.195	1.195	444	13
1.051	1.051	800	7
0.961	0.962	616	7
0.943	0.944	626	8
0.940	0.940	318	13
0.931	0.931	804	7
0.906	0.906	761	Weak
0.851	0.851	309	Weak
0.832	0.832	10, 1, 1	Weak
0.807	0.807 or 0.808	10, 2, 2 or 905	Weak

The magnetic susceptibility between 77 and 300°K is presented in Figure 1. Above 175°K, the compound has a temperature-independent paramagnetism. Below this temperature, Curie–Weiss behavior is observed. A small field dependence was observed both at room temperature and at liquid nitrogen temperature. Qualitative tests indicate that the compound is a good electrical conductor.

The X-ray diffraction pattern obtained at temperatures below 175°K did not reveal any change in structure.

Discussion

In view of the report that β-molybdenum nitride is stable only above 600°, it seemed likely that the compound we had prepared was stabilized by the inclusion of calcium or strontium in the lattice. One calcium ion per unit cell would correspond to about 1.3% calcium. Our chemical test should have detected this amount. The alkaline earth nitrides then appear to be acting as nitriding catalysts. The lower limit of the proportion of calcium nitride (Mo:Ca = 45) may depend on the amount required to make contact with each particle of molybdenum metal. Particle size and effectiveness of the mixing operation would be important factors to consider. No experiments of this kind were made.

The compound we have prepared is similar but perhaps not identical with that described by Hägg. Our preparations contained about 2.5 atom % more nitrogen. The observation of additional reflections in our diffraction patterns may have been due to the use of copper Kα radiation. Hägg used the longer wavelength chromium radiation and consequently may not have been able to detect the far-out reflections. It is these reflections which call for the larger unit cell and show that the structure is not face-centered tetragonal as Hägg reported. The departure from face-centered symmetry could be due to a slight displacement of the molybdenum atoms. A reasonable proposal for the structure is based on a slightly distorted cubic close packing of molybdenum atoms with about half of the octahedral sites occupied by nitrogen atoms. The nitrogens are probably in some ordered arrangement. For instance, the 14 nitrogens could be arranged at the centers of each of the eight pseudocells and at the centers of the six common edges. Slight displacement of some of the molybdenum atoms would be expected in this structure and would make difficult a structural analysis based on powder diffraction data.

The structural features proposed for this nitride would be consistent with the observed magnetic data. A small percentage of the molybdenum atoms in the lattice would be completely surrounded by nitrogens and would thus be isolated from interaction with other molybdenums. Most of the molybdenum atoms, however, would not be completely isolated, and metallic interaction between these molybdenums would be expected. The metallic molybdenum atoms should give rise to a temperature-independent paramagnetism which would dominate the magnetic characteristics of the nitride at higher temperatures. At lower temperatures, however, the paramagnetic moments associated with the isolated molybdenums would become dominant, and the magnetic behavior shown in Figure 1 would be observed.

There was no dramatic change in the electrical conductivity of the compound from room temperature to liquid nitrogen temperatures nor was any structural change noticed. Our examination of the properties at low temperatures, however, would have detected only gross changes. Further study of this phenomenon could yield significant information.

Acknowledgment.—This work was carried out with the support of a grant from the National Science Foundation. We have greatly appreciated the advice of Dr. Lewis Katz and Dr. A. F. Wells in the X-ray portion of this investigation. Thanks are also due to Dr. Carl Moeller for his assistance in the interpretation of magnetic data and to Dr. John Tanaka for his assistance in the design and construction of the vacuum equipment used in this investigation.

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Chlorine Perchlorate

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The new chlorine oxide, $ClOClO_3$, has been prepared in high yield by the reaction of either cesium perchlorate or nitronium perchlorate with chlorine fluorosulfate at −45°. Characteristic physical data are reported for the compound together with some of its chemical reactions. Chlorine monofluoride also reacts with perchlorates to form $ClOClO_3$ but in low yield.

Halogen fluorosulfates and peroxydisulfuryl difluoride have been shown to be effective in oxidizing a variety of anions[1-3] or in displacing halogen substituents from certain covalent species.[4] For example, $ClSO_3F$ can react[3] with AgCl to generate Cl_2 or with CsF to generate ClF and the respective metal fluorosulfate. The present investigation sought to take advantage of this type of interaction using perchlorate salts as the anionic substrates. It has been found that this reaction results in the formation of the new chlorine oxide, chlorine perchlorate

$$MClO_4 + ClSO_3F \longrightarrow MSO_3F + ClOClO_3 \quad (M = NO_2, Cs)$$

These reactions occur in high yield (75–95%) over a period of several days or less at approximately −45°.

Experimental Section

Apparatus and Materials.—The equipment used in this work has been described[3] and was supplemented with a Perkin-Elmer Infracord, Model 457. Cesium perchlorate (Matheson Coleman and Bell) and nitronium perchlorate (Callery Chemical Co.) were purchased and used without further purification. Chlorine fluorosulfate was prepared from ClF and SO_3 as reported previously.[3] Gaseous reactants were purified by fractional condensation. All handling of solids was performed in a dry nitrogen filled glove box. As a routine operation, all metal or Teflon equipment was passivated with ClF_3 before use.

Preparation of $ClOClO_3$.—In a typical experiment, a 30-ml stainless steel cylinder was loaded with 2.45 g (10.5 mmol) of $CsClO_4$. After evacuation, $ClSO_3F$ (218 cm^3, 9.73 mmol) was condensed into the cylinder at −196°. The reaction was allowed to proceed by maintaining the cylinder at approximately −45° for several days. The products were separated by fractional condensation in U traps cooled to −78, −112, and −196°. Little or no gases not condensable at −196° were found. The −196° fraction (8.0 cm^3, 0.36 mmol) was primarily Cl_2 with a small amount of SO_2F_2, while the −78° fraction was negligibly small. Pure $ClOClO_3$ (207 cm^3, 9.24 mmol) was retained at −112°. The yield was 95%. A similar reaction using NO_2ClO_4 (2.0 g, 13.7 mmol) and $ClSO_3F$ (200 cm^3, 8.93 mmol) produced $ClOClO_3$ (170 cm^3, 7.59 mmol) in 82% yield. The solid products from these reactions were identified as $CsSO_3F$–$CsClO_4$ and NO_2SO_3F–NO_2ClO_4 mixtures by their infrared spectra.[5-7] Synthetic reactions of this scale with either salt when terminated after 3–4 days were found to be complete with no detectable $ClSO_3F$ remaining. Normally, longer reaction times were used to ensure complete consumption of $ClSO_3F$ since its vapor pressure and that of $ClOClO_3$ are much too close to allow separation by a fractionation procedure. For the same reason, all preparations were conducted with excess perchlorate salt.

Properties of $ClOClO_3$.—Chlorine perchlorate is a pale yellow liquid and nearly white when frozen. It is stable for limited periods at room temperature in clean, dry, prepassivated stainless steel or perhalogenated plastic equipment. Storage at −45° in stainless steel cylinders has resulted in <1% decomposition per week over a 12-week period. Products of this low-temperature decomposition are Cl_2, O_2, and Cl_2O_6 which are readily separated from $ClOClO_3$.

Analysis.—Thermal decomposition of $ClOClO_3$ (91.0 cm^3, 4.06 mmol) in a stainless steel cylinder for 3 days at ambient temperature followed by 18 hr at 150° resulted in complete degradation to the elements: Cl_2 (90.8 cm^3, 4.05 mmol) identified by vapor pressure and gas chromatography and O_2 (181.0 cm^3, 8.08 mmol) identified by vapor pressure and mass spectroscopy. Therefore, the observed ratio of Cl_2:O_2 was 1.00:1.99 compared to the theoretical ratio of 1.00:2.00.

Molecular Weight.—Values for the molecular weight of $ClOClO_3$ as determined by gas density, assuming ideal gas behavior, were 133, 135, and 134 (calcd 135).

Vapor Pressure and Boiling Point.—The vapor pressure of $ClOClO_3$ over the temperature range −47 to 21° is [t (°C), P

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