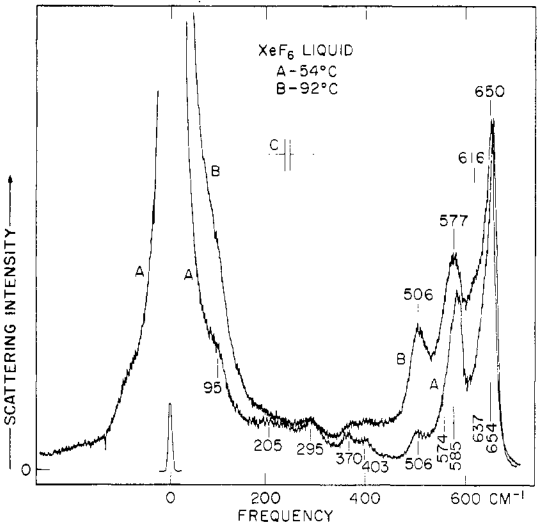

Figure 1.—Raman spectrum of liquid XeF_6: A, sample at 54°; B, sample at 92°; C, equivalent slit width.

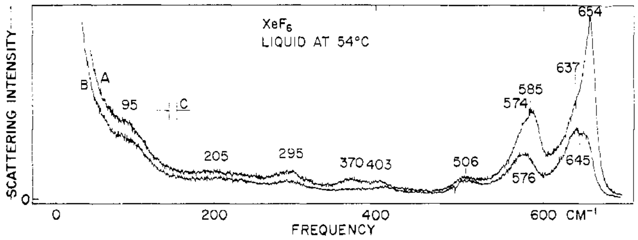

Figure 2.—Raman spectrum of liquid XeF_6 at 54°: A, incident polarization perpendicular; B, incident polarization parallel; C, equivalent slit width.

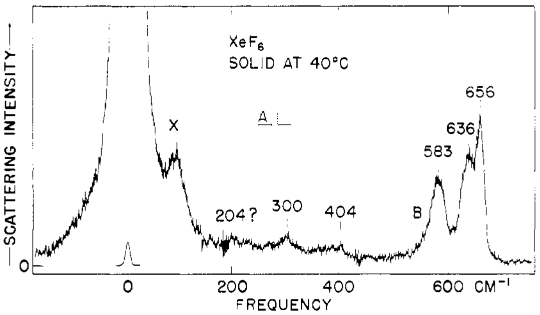

Figure 3.—Raman spectrum of solid XeF_6 at 40°.

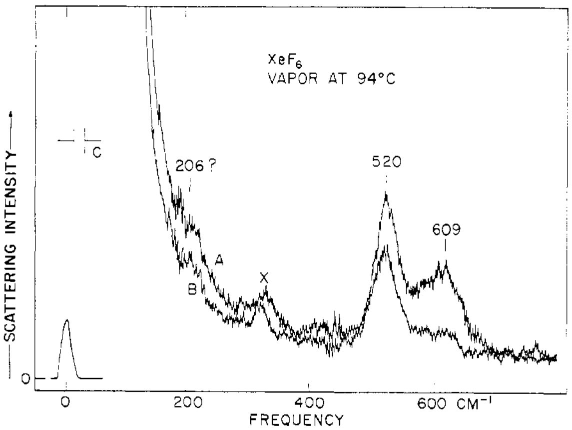

Figure 4 —Raman spectrum of XeF_6 vapor at 94°: A, incident polarization perpendicular; B, incident polarization parallel; C, equivalent slit width.

known to be essentially monomeric from vapor density measurements,[5] this band is shifted to 520 cm^{-1}.

Fifteen hexafluoride molecules had been studied before the preparation of XeF_6 and all had been found to have octahedral vapor molecules of symmetry O_h. Such molecules have three Raman-active fundamentals. They characteristically show up as a sharp, highly polarized band of highest frequency, a depolarized band 50–100 cm^{-1} lower, and a depolarized band of much lower frequency—assigned to species a_{1g}, e_g, and f_{2g}, respectively. The spectrum of XeF_6 vapor is similar to this pattern, but differs strikingly in that the highest frequency, polarized band is so broad. It is difficult to see how the "breathing" vibration of a symmetrical hexafluoride can show up in the Raman spectrum as anything but a sharp, line-like band.

The infrared spectrum of XeF_6 vapor shows two distinct absorption maxima in the bond-stretching region[1] at 613 and 520 cm^{-1}, whereas an O_h molecule has only one active stretching fundamental. Now it may be noted that there is a very close coincidence in frequency between infrared and Raman for both stretching bands.

These observations lead to the conclusion that either the ground-state vapor molecules possess a symmetry lower than O_h or they have some very unusual electronic properties that markedly influence the region of spectrum usually considered the vibrational–rotational region. Unfortunately, a more detailed conclusion cannot be given at the present time. The problem is one of unusual difficulty whose solution will require results from a wide variety of measurements, some of which have not yet been completed.

Acknowledgment.—We want to express appreciation to J. G. Malm, F. Schreiner, and D. W. Osborne for making available to us part of the sample of XeF_6 whose purity was indicated to be above 99.8% by melting temperature measurements.

(5) B. Weinstock, E. E. Weaver, and C. P. Knop, *Inorg. Chem.*, **5**, 2189 (1966).

CONTRIBUTION FROM THE RESEARCH DIVISION,
ROCKETDYNE, A DIVISION OF NORTH AMERICAN AVIATION, INC.,
CANOGA PARK, CALIFORNIA 91304

A New Synthesis of Chlorine Nitrate

BY CARL J. SCHACK

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Previous methods for the preparation of chlorine nitrate involve the reaction of either Cl_2O or ClO_2 with NO_2 or N_2O_5.[1] To circumvent the use of these hazardous chlorine oxides, a new route to this compound was sought as indicated by the equation

$$ClF + HNO_3 \longrightarrow ClNO_3 + HF$$

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[1] (a) H. Martin, *Angew. Chem.*, **70**, 97 (1958); (b) M. Schmeisser, *Inorg. Syn.*, **9**, 127 (1967).

It has been found that this reaction constitutes a rapid and convenient synthesis of chlorine nitrate. The reaction occurs on contact of the ClF with HNO_3 at temperatures down to −112° in 85–95% yield. The product $ClNO_3$ was purified by vacuum fractionation. The vapor pressure was measured over a considerably broader range (−80 to 26°) than that in the literature (−70 to −25°). The temperatures and vapor pressures are: −79.8°, 1 mm; −63.9°, 6 mm; −46.2°, 22 mm; −25.9°, 75 mm; 0.0°, 302 mm; 13.0°, 526 mm; and 26.1°, 866 mm. The vapor pressure–temperature relationship is described by $\log P(\text{mm}) = 7.9892 - (1509.4/T)$.

Chlorine nitrate has a boiling point of 22.3° (*vs.* literature extrapolation of 18°) with a heat of vaporization of 6.9 kcal/mole and a Trouton constant of 23.4. The compound is stable in stainless steel systems after pretreatment with some $ClNO_3$. Long-term storage in stainless steel or glass at approximately −40° has not resulted in any significant decomposition. Unlike FNO_3[2] and the chlorine oxides, no explosive incidents have been experienced with $ClNO_3$. However, the material should be handled with care in the absence of sensitivity test reports.

Experimental Section

Chlorine monofluoride and nominally anhydrous HNO_3 (distilled from H_2SO_4) were separately condensed at −196° into a stainless steel or Kel-F cylinder attached to a stainless steel–Teflon vacuum line. The cylinder was closed and the temperature was changed to some higher constant temperature in the range −112 to 0°. The reactor was then held at −78° and the product pumped out rapidly and trapped at −95°. Little or no HF was removed from the reactor in this manner as evidenced by the failure to generate SiF_4 when the product was subsequently handled in glass. Sometimes HF was removed by allowing the products to stand over NaF for a period. The identity of the product was established by its infrared spectrum[3] and molecular weight from vapor density measurements. Vapor phase chromatography, using a column packed with 50% w/w of Halocarbon oil 4-11V and Kel-F low-density molding powder according to Dayan and Neale,[4] gave an analysis of 98.4% $ClNO_3$ and 1.6% Cl_2. This sample was taken after 2 days in the metal vacuum system at temperatures up to ambient temperature. The Cl_2 impurity is a decomposition product which probably arose during this period or subsequent handling in the gas chromatograph. For the purpose of determining the stoichiometry, the more accurately measurable ClF was used as the limiting reagent. Typically, 11.9 mmoles of ClF was allowed to react with approximately 14 mmoles of HNO_3 and yielded 10.6 mmoles of $ClNO_3$ (89%). In an alternative procedure, the HNO_3 was maintained at −78° while ClF gas was gradually admitted to the reactor. When the pressure ceased to drop, the reaction was complete. Work-up was as above. The synthesis has been successfully conducted on a scale of several liters.

Acknowledgment.—This work was supported by the Office of Naval Research, Power Branch.

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[2] W. Kwasnik, "Handbook of Preparative Inorganic Chemistry," Vol. I, G. Brauer, Ed., Academic Press Inc., New York, N. Y., 1963, p 189.

[3] K. Brandle, M. Schmeisser, and W. Luttke, *Chem. Ber.*, **93**, 2300 (1960).

[4] V. H. Dayan and B. C. Neale, Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p 223.

Correspondence

Structural *vs.* Ligand Field Strength Effects on Covalency in Pseudo-Tetrahedral Complexes of Cobalt(II) and Nickel(II) Dihalides, as Determined by Proton Magnetic Resonance

Sir:

There have appeared recently a number of publications[1-6] concerning the proton magnetic resonance shifts for pseudo-tetrahedrally coordinated cobalt(II) and nickel(II) dihalide complexes, abbreviated $L_2M^{II}X_2$, where X = Cl, Br, or I, and L = pyridine-type ligand, py;[4-6] triarylphosphine, $(\text{aryl})_3P$;[1-3] or hexamethylphosphoramide, HMPA.[6] Most of the attention has been focused on ascertaining the ligand orbital containing the unpaired spin.[1,3,5,6] For some of these complexes, it has been observed[3,6] that the contact shifts and hence presumably also the extent of spin delocalization from the metal depend upon the halide ion, increasing in the order Cl < Br < I. To explain this effect, Wayland and Drago[6] invoked a molecular orbital picture of the complexes, where the metal dihalide fragment for variable halogen would have antibonding orbitals of varying energy, Cl > Br > I, reflecting their ligand field strengths, such that when the neutral ligands are added, the extent of metal–ligand covalency increases Cl < Br < I.

However, an important factor was neglected in this analysis,[6] this being that there is no assurance that the structure of a complex is invariant for different halides. In the absence of proof for identical structures, the observed trends cannot be taken as evidence for an electronic anion effect. Indeed, X-ray work on $((\text{phen})_3P)_2NiCl_2$ has shown[7] that both the Cl–Ni–Cl and P–Ni–P angles deviate appreciably from 109°, having been attributed to differences in ligand–ligand repulsions,[7] though other effects could also be operative. In view of the fact that halide–halide repulsions vary, the

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[1] G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

[2] G. N. La Mar, *ibid.*, **41**, 2992 (1964).

[3] E. A. LaLancette and D. R. Eaton, *J. Am. Chem. Soc.*, **86**, 5145 (1964).

[4] E. E. Zaev, G. I. Skubnevskaya, and Y. N. Molin, *J. Struct. Chem.*, **6**, 610 (1965).

[5] R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **88**, 1071 (1966).

[6] B. B. Wayland and R. S. Drago, *ibid.*, **88**, 4597 (1966).

[7] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).