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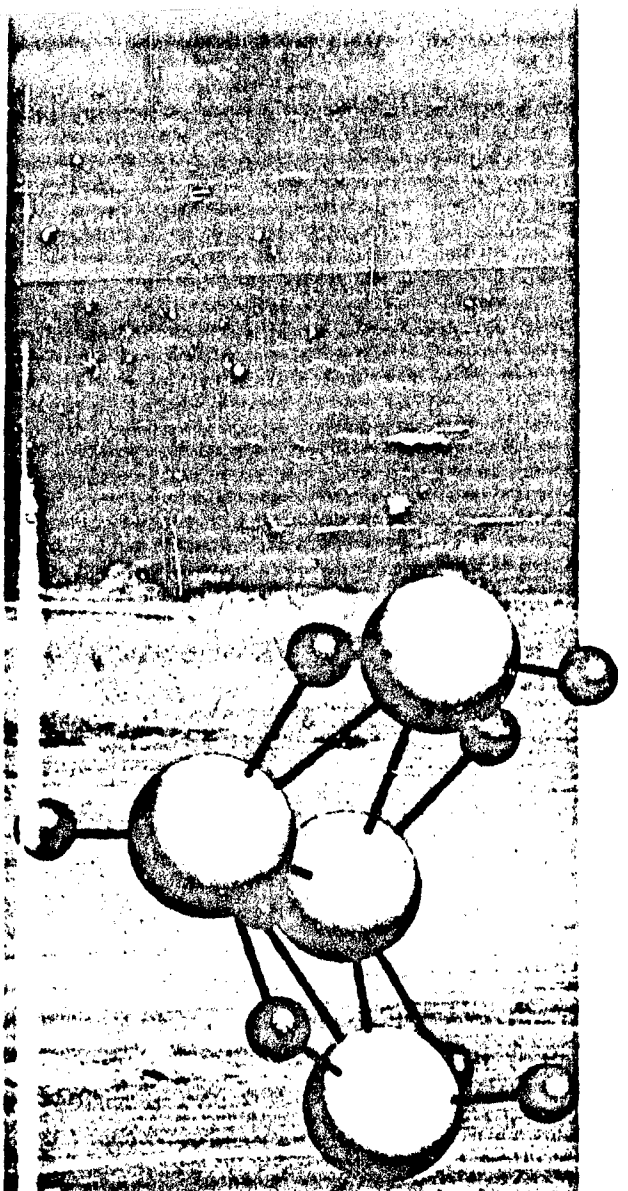

FINAL REPORT

STUDIES OF COMPLEX PERCHLORATES

ONR Nonr 3943(00)

June 1, 1966

CALLERY CHEMICAL COMPANY

STUDIES OF COMPLEX PERCHLORATES

ONR Nonr 3943(00)

FINAL REPORT

by

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June 1, 1966

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FOREWORD

The following manuscripts of five papers constitute the final report for Contract NOnr 3943(00). Papers I and V have been published. Papers II, III and IV consists of a series of publications on complex perchlorate derivatives, the first of which (II) is in final form for publication. Paper III and IV are drafts of publications which may be subject to minor alterations.

An appendix contains information on the hexanitratoaluminate ion which, although insufficient for publication, is significant and pertinent to the publishable information.

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I. RAMAN AND INFRARED SPECTRA OF NITRONIUM PERCHLORATE

Inorganic Chemistry, 4, No. 12, 1796 (1965)

J. W. Nebgen,[a] and A. D. McElroy[b] and H. F. Klodowski[c]

Abstract

The Raman spectrum of crystalline nitronium perchlorate exhibits ten well resolved lines plus an additional tentative line appearing as a weak shoulder. The infrared spectrum, with sodium chloride optics, contains moderately intense absorptions at 940 cm^{-1} and 2300 cm^{-1} and a strong broad absorption in the region of 1100 cm^{-1} which shows some tendency to resolve into three peaks. The spectra have been interpreted in terms of structural features shown by X-ray structure data. In addition, an interpretation is given correlating the bending mode of the nitronium ion with cation-anion interaction in crystalline nitronium salts.

(a) Midwest Research Institute
(b) Presently at Research Institute, work performed at Callery Chemical Company
(c) Callery Chemical Company

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INTRODUCTION

Nitronium perchlorate has classically been considered to be an ionic compound, with discrete nitronium ions and perchlorate ions. Evidence of its ionic character is well documented in the literature. Infrared data[1] and Raman spectra[2] are generally what should be expected of a linear NO_2^+ ion isoelectronic with CO_2, and a tetrahedral ClO_4^- ion. We have obtained a more highly resolved Raman spectrum of nitronium perchlorate which cannot be interpreted using a model of isolated linear nitronium ions and isolated tetrahedral perchlorate ions. Our infrared data and those of earlier workers[1] are generally consistent with one another. The spectral data for solid nitronium perchlorate are listed in Table I along with assignments of vibrational modes.

X-ray investigations[3] have shown that in nitronium perchlorate the NO_2^+ ion is slightly nonlinear and ClO_4^- is similarly distorted from a tetrahedron. These facts and other features of the crystal structure have been correlated with the observed spectra using the rigorous theory of vibrations in crystals[4,5]. This analysis has shown that our spectral data are consistent with basic aspects on the crystal structure. Examination of existing information about other nitronium salts has, in addition, revealed fundamental differences in the character of the nitronium ion as it exists in different compounds.

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(1) J. R. Soulen and W. F. Schwartz, J. Phys. Chem., 66, 2066 (1962).
(2) D. J. Millen, J. Chem. Soc., 2606 (1950).
(3) M. R. Truter, D. W. J. Cruikshank and G. A. Jeffrey, Acta Cryst., 13, 855 (1960).
(4) R. S. Halford, J. Chem. Phys., 14, 8 (1946).
(5) D. F.Hornig, J. Chem. Phys., 16, 1063 (1948).

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TABLE I

INFRARED AND RAMAN FREQUENCIES OBSERVED IN NITRONIUM PERCHLORATE

Frequencies Observed (cm^{-1})		Frequencies Reported From Other Sources (cm^{-1})		
Infrared	Raman	Infrared[a]	Raman[b]	
	448		461	Symmetric ClO_4^- bend
	471			
	571	570		NO_2^+ bend
	625	625	626	Antisymmetric ClO_4^- bend
	640			
	642 sh(?)			
940	936	936	937.8	Symmetric ClO_4^- stretch
1060?	1080		1082	Antisymmetric ClO_4^- stretch
1080?	1095	1100 vb		
1130	1139		1143	
	1396		1396.2	Symmetric NO_2^+ stretch
2360		2360		Antisymmetric NO_2^+ stretch

(a) Reference 1.

(b) Reference 2.

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EXPERIMENTAL

Crystalline nitronium perchlorate as produced by Callery Chemical Company was employed in the studies. Samples were handled in a dry box atmosphere, with exposure even to a dry atmosphere being minimized as much as possible.

Raman Spectra. -- The most highly resolved spectra were obtained with crystals approximately 1 mm. in diameter. Finely divided powder and crystals yielded spectra with the same features, but the best signal to noise ratio was found with larger particles. Spectra were obtained with a Cary Model 81 spectrometer without rearrangement of instrument optics.

Various types of sample holders were investigated. The holder which gave the best response and resolution is worthy of special mention, as it has not apparently been described in the literature. Sample holders were constructed of Pyrex tubing of the same outside diameters as liquid sample holders supplied for the instrument. A standard taper joint was sealed to one end of the holder. The other end of the tube contained a conically shaped configuration which held the sample. One method of construction consisted of fabricating a test tube end which was then indented (Vigreau type indentation) by means of a carbon rod with a conically shaped tip. The cone and tube were coaxial, and the height of the cone was 1 to 1.5 times the diameter of the tube. The radius of the cone varied from less than 1 mm. at the tip to slightly less than the inside radius of the tube. The sample of nitronium perchlorate, 1 to 2 g., was contained in the space between the tube

and the cone, so that varying thicknesses of sample were exposed to incident radiation. Some holders were equipped with a hollow tubular extension about 3 in. long, which was sealed to the end of the tube containing the cone. The extension was painted black, and its end fitted flush against the cell optics. The latter arrangement generally gave stronger signals. The spectrum of nitronium perchlorate presented in Figure 1 was obtained, however, with a 22 mm. O.D. sample holder with the base of the cone flush against the cell optics.

Infrared Spectra. -- Finely divided powders or Nujol mulls were dispersed thinly between two paired windows of sodium chloride and various other available materials. The best spectra were obtained with barium fluoride windows. The windows were sealed as tightly as possible with pressure sensitive tape. Spectra were recorded with a Perkin-Elmer Infracord; resolution was sacrificed for speed, since the appearance of most spectra changed within a matter of minutes. The changes in the spectra with time are attributed primarily to unavoidable hydrolysis. Exposed samples exhibited a single sharp, strong band peaking at about 1100 cm^{-1}, and very weak absorptions at 2360 cm^{-1} and 940 cm^{-1}. The 2360 cm^{-1} and 940 cm^{-1} absorptions were sharp and of moderate intensity in the best spectra of freshly prepared samples (Table I) and a strong broad absorption occurred between about 1150 cm^{-1} and 1000 cm^{-1}. This broad band peaked fairly sharply at 1130 cm^{-1}, and exhibited evidence of weakly resolved peaks at 1100 - 1080 cm^{-1} and 1060 - 1030 cm^{-1}.

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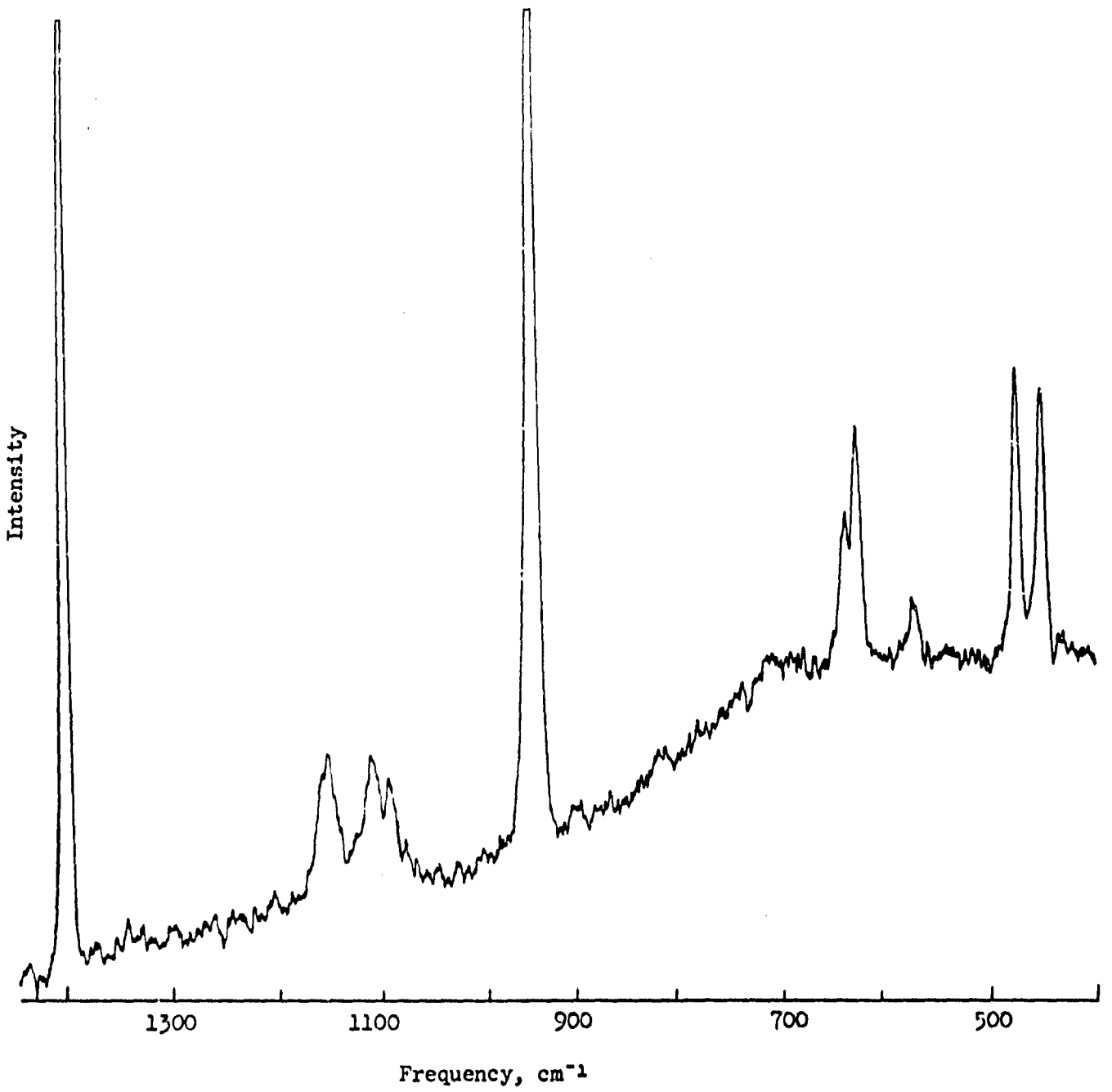
FIGURE I

SPECTRUM OF NITRONIUM PERCHLORATE



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DISCUSSION

Nitronium perchlorate crystallizes in a monoclinic unit cell (space group $C/2c\text{-}C_{2h}^{6}$) containing four formula units[3]. The crystal contains discreet units of nitronium cation (NO_2^+) and perchlorate anion (ClO_4^-). The nitrogen and chlorine nuclei are located on twofold axes within the unit cell, and the two ions are alternately spaced along these axes. The location of these atoms in the unit cell requires that the two oxygens in the nitronium ion be equivalent (but not necessarily colinear with the nitrogen nucleus), and that the four oxygens in the perchlorate ion be divided into two pairs which are not necessarily equivalent. This condition permits the observed bend (ca. 5°) in the NO_2^+ cation, and the observed distortion in the ClO_4^- anion.

Consider first the transitions due to the nitronium ion. An isolated linear nitronium ion would be expected to exhibit three vibrations. The non-degenerate symmetric stretching mode would be Raman active. The non-degenerate antisymmetric stretching mode and the doubly degenerate bending mode would both be infrared active. Since there is a center of symmetry in the species, dual Raman and infrared activities are not permitted. In the crystal, on the other hand, symmetry would cause each of these vibrations to become both Raman and infrared active, and the degenerate bending mode to become split. However, since the nitronium ion is bent in its equilibrium configuration in crystalline nitronium perchlorate, only one bending mode would be expected in both the Raman and infrared spectra.

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The infrared absorption at 2360 cm^{-1} and the Raman line at 1396 cm^{-1} clearly belong to the antisymmetric and symmetric stretching vibrational modes respectively. The absence of a Raman transition near 2360 cm^{-1} and an infrared band near 1400 cm^{-1} shows that the stretching modes do not exhibit dual activity. However, a weak line appears at 571 cm^{-1} in the Raman spectrum and a strong band at 570 cm^{-1} in the infrared[1]. The exactness of these frequencies, plus the fact that a vibration due to ClO_4^- has never been reported in this area, leads us to the conclusion that this frequency is the NO_2^+ bend in both spectra.

The lack of dual activity for the stretching motions cannot be used to dispute this interpretation, since the theory of Raman and infrared transitions in crystals[4,5] can only predict the numbers and activities of observed transitions. On the basis of symmetry alone, theory cannot predict the positions or the intensities of these components.

Let us now consider the perchlorate ion. In solutions of perchlorate compounds, four vibrations corresponding to a simple tetrahedral configuration are observed[6]. The non-degenerate breathing vibration at 935 cm^{-1} and the doubly degenerate in-phase bending vibration at 462 cm^{-1} are both Raman active but not infrared active. The remaining two vibrations are the triply degenerate modes at 1082 cm^{-1} and 628 cm^{-1} corresponding to the antisymmetric stretching and bending motions, respectively. These two vibrations are active in both the Raman and infrared. Since symmetry permits two non-equivalent pairs of oxygen

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(6) G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, D. VanNostrand Company, Inc., Princeton, N. J., 1945, p. 167.

in the ClO_4^- anion, the degenerate vibrations should be split into individual components, and all vibrations should become both infrared and Raman active. Thus we should see nine fundamentals with both techniques. The triply degenerate vibrations should give a group of three lines, and the doubly degenerate vibrations should give rise to two. The non-degenerate breathing mode should be observed as a singlet in both spectra. As can be seen from Table I, this pattern is followed closely.

The strong line at 936 cm^{-1} in the Raman and the weak band at 940 cm^{-1} in the infrared are due to the symmetric breathing vibration of the perchlorate ion. The two transitions at 448 cm^{-1} and 471 cm^{-1} in the Raman spectra arise from the doubly degenerate in-phase bending of the perchlorate ion. Infrared data are not available for these low lying vibrations. However, one would expect a weak doublet, or more likely a weak, unresolved absorption. The group of three vibrations at 1080 cm^{-1}, 1095 cm^{-1} and 1139 cm^{-1} in the Raman spectrum, and the broad absorption region around 1100 cm^{-1} in the infrared arise from the triply degenerate antisymmetric stretching mode of the ClO_4^- anion.

Finally, we come to the triply degenerate antisymmetric bending mode for the ClO_4^- anion. In the infrared[1], this transition is observed as a band at 625 cm^{-1} with a shoulder on the high frequency side. In the Raman, it appears as a doublet at 625 cm^{-1} and 640 cm^{-1}. Theory says that this mode should appear as a group of three separate transitions. The question immediately arises whether the Raman band at 571 cm^{-1} is the third component of the perchlorate antisymmetric bend, or whether it indeed belongs to the NO_2^+ species where we have assigned it. The shift from 628 cm^{-1} in tetrahedral perchlorate[6] to

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571 cm^{-1} is very large, and it is highly questionable whether this large shift can be attributed to resolution of degeneracy. A close examination of the Raman spectrum reveals a small shoulder on the high frequency side of the 640 cm^{-1} band which might account for the missing third frequency.

Fundamental Implications. -- The Raman spectrum of nitronium perchlorate is strikingly similar to spectra observed by Hathaway and Underhill[7] for certain transition metal perchlorates. These authors advanced an explanation involving a bidentate ClO_4 group, and their treatment implies structures substantially covalent in nature. Nitronium perchlorate is clearly ionic, and one must interpret its spectra in terms of ions. It is apparent that interpretations of bonding on the basis of symmetry alone must be made with caution. The X-ray and spectral data for nitronium perchlorate are nevertheless indicative of an interaction between cation and anion. In nitronium perchlorate we have a relatively rare case in which spectra are capable of indicating change in both cation and anion, and the data should therefore be examined for evidence of the nature of bonding in crystalline ionic compounds.

Additional insight can be gained from considerations of NO_2^+ in other salts and of the isoelectronic carbon dioxide molecule in the solid state. Pertinent data are available for nitronium nitrate (infrared[8], Raman[9], and structure by X-ray[10]) and nitronium fluoborate (Raman and infrared[11]).

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(7) B. J. Hathaway and A. E. Underhill, J. Chem. Soc., 3091 (1961).
(8) R. Teranishi and J. C. Decius, J. Chem. Phys., 22, 896 (1954).
(9) J. Chedin, Compt. Rend., 201, 552 (1935).
(10) E. Grison, K. Eriks and J. L. deVries, Acta Cryst., 3, 290 (1950).
(11) J. C. Evans, H. W. Rinn, S. J. Kuhn and G. A. Olah, Inorg. Chem., 3, 857 (1964).

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The fundamental frequencies of the nitronium ions and carbon dioxide are presented in Table II. While the stretching frequencies are very nearly identical in all cases, the only NO_2^+ bending mode closely equal to that of carbon dioxide is that of nitronium fluoborate (doublet centered at 598 cm^{-1}). In nitronium perchlorate and nitronium nitrate, the bending modes are shifted to lower frequencies (570 cm^{-1} and 538 cm^{-1}, respectively). These shifts clearly indicate decreased resistance to bending. This transformation is accomplished with little effect on nitrogen-oxygen bonding energies, as the stretching frequencies are almost identical for all four cases.

It can be inferred from the above comparisons that NO_2^+ bending frequencies are a measure of the extent of interaction, in crystals, between the nitronium cation and companion anion. In nitronium fluoborate little cation-anion interaction is indicated, and one predicts a linear NO_2^+ ion. On this basis, NO_2^+ in nitronium fluoborate is deemed to be more completely ionic than in nitronium perchlorate and nitronium nitrate. The cation of nitronium nitrate is by the same reasoning the least ionic; this conclusion is supported by the ease with which this compound volatilizes and reverts to appropriate covalent species.

Walsh[12] has shown that addition of an electron to NO_2^+ should theoretically be accompanied by the observed change in angle from 180° to 143°. The small change in angle observed in nitronium perchlorate can therefore be

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(12) A. D. Walsh, J. Chem. Soc., 2266 (1953).

TABLE II

INFRARED AND RAMAN FREQUENCIES IN VARIOUS NITRONIUM SALTS AND SOLID CARBON DIOXIDE (cm^{-1})

NO_2ClO_4		NO_2NO_3		NO_2BF_4		CO_2 (s)		
IR	Raman	IR[a]	Raman[b]	IR[c]	Raman[c]	IR[d]	Raman[e]	
570	571	538	-	590 605	-	653 660	-	ν_2, bending mode
-	1396	-	1400	-	1399	-	1388	ν_1, symmetric stretching mode
2360	-	2375	-	2380	-	2344	-	ν_3, antisymmetric stretching mode

(a) Reference 8.

(b) Reference 9.

(c) Reference 11.

(d) W. E. Osberg and D. F. Hornig, J. Chem. Phys., 20, 1345 (1952).

(e) J. C. McLannan and H. D. Smith, Can. J. Res., 7, 551 (1932).

(f) Reference 1.

considered to result from a partial transfer of charge from perchlorate ion to nitronium ion. The transferred charge would be concentrated on the nitrogen atom, and would not be expected to contribute significantly to the nitrogen-oxygen bond energy. Thus, the stretching frequencies should remain unchanged. On the other hand, the additional charge on the nitrogen atom would significantly affect the bending frequency. In nitronium nitrate, linearity is enforced by crystal symmetry, and the excess charge is evidenced only by a lowering of the bending frequency.

The proposed partial charge transfer can be treated as a resonance phenomenon, which implies a contribution of neutral NO_2 and neutral ClO_4 species to the over-all wave function of the crystal. This minor contribution is exclusive of those for the individual NO_2^+ cations and ClO_4^- anions. From a molecular orbital point of view, the model implies a small overlap between orbitals of the nitronium and perchlorate ions. The overlap would be much too small to interpret as covalency. Our interpretation presents a picture of the observed interactions which is consistent with the concept that ionic crystals are inadequately described by purely electrostatic forces.

Acknowledgment. -- Support of this research by the Office of Naval Research is gratefully acknowledged.

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II. COMPLEX LIGHT METAL PERCHLORATES - TETRAPERCHLORATOALUMINATES

C. R. Guibert, H. F. Klodowski, M. D. Marshall and A. D. McElroy

Abstract

Two complex perchlorates of aluminum, $NO_2Al(ClO_4)_4$ and $NH_4Al(ClO_4)_4$, have been prepared and characterized. Nitronium tetraperchloratoaluminate is synthesized by reaction of aluminum chloride in liquid sulfur dioxide with four moles of nitronium perchlorate. The same technique yields ammonium tetraperchloratoaluminate if one of the four moles of nitronium perchlorate is replaced by ammonium perchlorate. The compounds are white to yellow solids readily soluble in sulfur dioxide, and are stable to about 50°C. Evidence relevant to the structure of these compounds indicates that they are tetracoordinate complexes of aluminum containing the anion $Al(ClO_4)_4^-$.

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INTRODUCTION

The perchlorate group is well known in ionic compounds typified by ammonium perchlorate. Compounds with acknowledged covalent bonding are few, including the anhydrous acid and unstable alkyl perchlorates. Anhydrous perchloric acid is notable for its tendency to extract water from itself, thereby generating hydronium perchlorate, a stable, salt-like compound. Anhydrous perchlorates of the multiply charged metallic cations which exhibit covalency in other compounds are rare. Exceptions ai the well known chromium (III) perchlorate and the recently reported perchlorates of boron.[1] Chromium (III) perchlorate can decompose with violence. The perchlorates of boron were stable only at reduced temperatures, though $(CH_3)_3N{\cdot}B(ClO_4)_3$ was described as quite stable. Anhydrous aluminum perchlorate was reported in early literature[2], but contemporary efforts to prepare this compound have not been successful. The lack of success encountered in efforts to prepare anhydrous perchlorates of multiply charged cations can be attributed to extraction of oxide by the cation. The metal-oxygen bond thus appears to exert a strong distortional effect on the ClO_4 group, with the result that decomposition occurs.

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(1) R. A. Mosher, E. K. Ives and E. F. Morello, J. Am. Chem. Soc., 85, 3037 (1963).
(2) E. Moles and J. Gonzalez de Barcia, Anales soc. espan, fis. quim., 34, 802 (1936).

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The highly ionic property of the perchlorate group is strongly supported by its reluctance to act as a coordinating ligand[3], and further by the lack of reported compounds in which the anion formally could be considered to be a ligand, though not necessarily coordinate-covalently bonded.

Several recent investigations have, however, given evidence suggestive of covalent character in several perchlorates. Hathaway and Underhill[4] observed departures from the T_d symmetry of the isolated tetrahedral ion in perchlorates of copper, nickel, cobalt and iron. In $Zn(ClO_4)_2 \cdot 4CH_3CN$, for example, the symmetry C_{3v} is indicated by the infrared spectrum, and Hathaway and Underhill suggest that perchlorate is weakly coordinated as a monodentate ligand. The symmetry C_{2v} was observed for anhydrous copper perchlorate, consistent with coordination as a bidentate ligand. Wickenden and Krause[5] reported similar spectroscopic evidence of monodentate coordination in $Ni(ClO_4)_2 \cdot 4CH_3CN$, and of bidentate coordination in $Ni(ClO_4)_2 \cdot 2CH_3CN$. Nebgen[6] has proposed some covalency as an explanation of reduced ClO_4 symmetry in nitronium perchlorate. Ross[7] observed lowered symmetry, usually to C_{2v}, in several perchlorates, including potassium perchlorate and ammonium perchlorate; he concluded, however, that covalent bonding was not contributing to any great extent, and that lowered symmetries were primarily a consequence of lattice distortional effects.

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(3) J. C. Bailar, "The Chemistry of the Coordination Compounds," p. 28, Reinhold Publishing Corporation, New York, 1956.
(4) B. J. Hathaway and A. E. Underhill, J. Chem. Soc., 3091 (1961).
(5) A. E. Wickenden and R. A. Krause, Inorg. Chem., 4, 404 (1965).
(6) J. W. Nebgen, A. D. McElroy and H. F. Klodowski, "Raman and Infrared Spectra of Nitronium Perchlorate," Inorg. Chem., in press.
(7) S. D. Ross, Spectrochimica Acta, 18, 225 (1962).

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One concludes that symmetry alone is not sufficient evidence of covalency, or of the formation of coordinate-covalent bonds. The fundamental frequencies of ClO_4^- are considerably more strongly split in anhydrous copper perchlorate[4] and in $Ni(ClO_4)_2 \cdot 2CH_3CN$[5] than in the classically ionic ammonium perchlorate[7] and nitronium perchlorate[6], however. On this basis it is reasonable to assume that the stronger distortional forces observed in copper perchlorate, as one example, may result from relatively strong metal-oxygen bonds. Cotton and Weaver[8] have very recently reported crystallographic and spectroscopic evidence for bis(2,5-dithiahexane) cobalt(II) perchlorate which shows that the perchlorate ion is indeed coordinated to cobalt. Of particular significance is the fact that the Co-$OClO_3$ bond distance is about 0.1 Å greater than in usual Co-O covalent bonds. This evidence dispels doubt concerning the possibility of coordinating the perchlorate ion, though the questions of bond strengths and of the precise nature of bonding remain unanswered.

We wish to report the preparation of two novel perchlorates of aluminum of the type $MAl(ClO_4)_4$. Properties of these compounds are consistent with their representation as $M^+(Al(ClO_4)_4)^-$. Formally, one mole of perchlorate ion has added to aluminum perchlorate, and in this context the perchlorate ion has acted as a coordinating ligand. Combined evidence supports representation of the new substances as true coordinate complexes.

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(8) F. A. Cotton and D. L. Weaver, J. Am. Chem. Soc., 87, 4189 (1965).

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EXPERIMENTAL

Reaction solvent. -- The need for a very weakly coordinating solvent is self-evident. The perchlorate ion is by all standards too weak a coordinating ligand to compete with usual basic solvents. Liquid sulfur dioxide served admirably as a preparative solvent, in spite of low solubilities of reactant perchlorates[9] (NO_2ClO_4, NH_4ClO_4, $KClO_4$ and $AgClO_4$), and exhibited no tendency to be retained by products. Aluminum-containing reactants ($AlCl_3$, $MAlCl_4$), were readily soluble in liquid sulfur dioxide, and preparative reactions proceeded to completion in an hour or two.

Reagents. -- Aluminum chloride was sublimed prior to use. In some instances aluminum chloride was allowed to react with ammonium or potassium chloride in sulfur dioxide, yielding the complex salts, $MAlCl_4$, which were then isolated and used as starting reagents. Nitronium perchlorate (99+%) was used as produced by Callery Chemical Company without further purification. Ammonium perchlorate and potassium perchlorate (Fisher Scientific, certified reagent grade) were dried in vacuo at 110°C. Silver perchlorate (G. F. Smith Chemical Comapny, anhydrous, 99+%) was redried in vacuo at 80°C.

Preparative procedures. -- Procedures employed are illustrated by Eqs. I, II, III and IV.

$$4NO_2ClO_4 + AlCl_3 \longrightarrow 3NO_2Cl + NO_2Al(ClO_4)_4 \qquad \text{I}$$

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(9) L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," p. 212, John Wiley and Sons, Inc., New York, 1953.

$$3NO_2ClO_4 + NH_4ClO_4 + AlCl_3 \longrightarrow 3NO_2Cl + NH_4Al(ClO_4)_4 \qquad II$$

$$4NO_2ClO_4 + NH_4AlCl_4 \longrightarrow 4NO_2Cl + NH_4Al(ClO_4)_4 \qquad III$$

$$4AgClO_4 + NH_4AlCl_4 \longrightarrow 4AgCl + NH_4Al(ClO_4)_4 \qquad IV$$

With methods I, II and III, by-product nitryl chloride was removed by volatilization along with sulfur dioxide. With method IV, by-product insoluble silver chloride was removed by filtration. The complex perchlorates were quite soluble in sulfur dioxide. Two typical experiments are described below.

Aluminum chloride (1.8 g) and nitronium perchlorate (8.0 g) were placed in a round bottom flask and 15 ml. of sulfur dioxide was added by condensation. At -78°C the solution was cloudy, and a clear, slightly yellow color resulted on warming to -10°C with stirring. After stirring two hours at -10°C the solution was filtered. A slight residue remained on the frit, and 6.3 g. (98% yield) of a white crystalline solid was obtained by evaporation of volatiles. Theory for $NO_2Al(ClO_4)_4$: Al, 5.73; N, 2.97; Cl, 30.1. Found: Al, 5.77; N, 3.29; Cl, 29.5.

Aluminum chloride (0.30 g), ammonium perchlorate (0.27 g) and nitronium perchlorate (0.99 g) were stirred in 15 ml. of sulfur dioxide for one hour at -10°C. A clear solution formed almost immediately. The solution was filtered, and 0.88 g. (89% yield) of product was recovered after evaporation of volatiles from the filtrate. Theory for $NH_4Al(ClO_4)_4$: Al, 6.09; N, 3.16; Cl, 32.0. Found: Al, 6.18; N, 3.62; Cl, 30.9.

Attempts to prepare anhydrous aluminum perchlorate by reaction in sulfur dioxide of one mole of aluminum chloride with three moles of nitronium

perchlorate or silver perchlorate failed. With silver perchlorate the Al:ClO_4 ratio in products was of the order of 1:2, and analyses for Al, Cl^- and ClO_4^- accounted for only about 85% of sample weights. The products obtained from nitronium perchlorate apparently consisted of $NO_2Al(ClO_4)_4$ admixed with oxyperchlorates or oxynitrates of aluminum.

Attempts to prepare $KAl(ClO_4)_4$ in good purity were unsuccessful. Reactions by methods II, III and IV proceeded readily, and yielded soluble products. Displacement of chloride was essentially complete, and the desired ratio fo 1K:1Al was found in products. For some reason not presently understood, ratios no better than 1Al:3.5 ClO_4 were observed.

In several experiments the initial charges consisted of equimolar quantities of aluminum chloride and ammonium or potassium perchlorate. The insoluble perchlorates were readily solubilized in sulfur dioxide by aluminum chloride. This fact can be construed as evidence of intermediate complexes of the type $M^+ClO_4AlCl_3^-$. These products have not been isolated for characterization. It is felt that such complexes may indeed exist, though disproportionation to $MAl(ClO_4)_4$ and $MAlCl_4$ may occur readily.

Properties of complex perchlorates. -- In addition to ready and high solubility in liquid sulfur dioxide, $NO_2Al(ClO_4)_4$ and $NH_4Al(ClO_4)_4$ dissolve readily in liquid phosgene and nitromethane. The solubility contrasts with a very low solubility exhibited by ammonium perchlorate and nitronium perchlorate. Solids recovered from nitromethane retain some solvent which cannot be removed by room temperature evacuation.

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The two new compounds appear to be stable indefinitely at ambient temperatures. At about 50°C, the unique X-ray diffraction pattern of $NO_2Al(ClO_4)_4$ is slowly displaced by a second unique pattern. As prepared, $NH_4Al(ClO_4)_4$ is amorphous to X-radiation, and this compound slowly becomes crystalline at about 50°C. Pronounced exotherms were observed by differential thermal analysis at 111°C for $NO_2Al(ClO_4)_4$ and at 88°-103°C for $NH_4Al(ClO_4)_4$.

Standard heats of formation were determined by measurements of heats of hydrolysis, and densities by displacement with Kel-F oil. $NO_2Al(ClO_4)_4$: ΔH_f^o = -110 ±5 kcal/mole, d = 2.34 g/cc; $NH_4Al(ClO_4)_4$: ΔH_f^o = -202 ±4 kcal/mole, d = 2.20 g/cc. Neither compound was sensitive to impact within the limits (300 kg. cm.) of the tester. Both are quite hygroscopic in air. Qualitative tests with $NO_2Al(ClO_4)_4$ indicated a reactivity with organic materials similar to that of nitronium perchlorate. The reactivity of $NH_4Al(ClO_4)_4$ was considerably lower, but it should be classified as a potent oxidizing agent.

The Raman and infrared spectra of $NO_2Al(ClO_4)_4$ are shown in Table I. Techniques for obtaining spectra have been discussed previously[6].

The apparent molecular weights of $NH_4Al(ClO_4)_4$ and $NO_2Al(ClO_4)_4$ in sulfur dioxide were determined by the freezing point depression method. Pertinent data are listed in Table II.

TABLE I

SPECTRA OF $NO_2Al(ClO_4)_4$

Infrared	Raman*	Assignment
	460 (16)	Symmetric ClO_4^- bend
	635 (14) 680 (9)	Antisymmetric ClO_4^- bend
925 sb	970 (25)	Symmetric ClO_4^- stretch
1040 s 1190 s, vb 1280 sh		Antisymmetric ClO_4^- stretch
	1400 (22)	Symmetric NO_2^+ stretch

* Numbers in parentheses indicate relative intensities.

TABLE II

MOLECULAR WEIGHTS BY FREEZING POINT DEPRESSION OF SULFUR DIOXIDE*

$NO_2Al(ClO_4)_4$: Formula weight, 471

Solute, g.:	0.8059	0.6098	0.4091	0.3068	0.2011
Molality:	0.118	0.0890	0.0598	0.0449	0.0294
M.W.:	502	482	462	474	415

$NH_4Al(ClO_4)_4$: Formula weight, 443

Solute, g.:	0.7819	0.5988	0.4292	0.3018	0.2143
Molality:	0.122	0.0930	0.0668	0.0470	0.0334
M.W.:	276	263	249	263	282

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* Freezing point depression constant, $K_f = 2.804°$ mole^{-1}.

DISCUSSION

The new compositions, $NH_4Al(ClO_4)_4$ and $NO_2Al(ClO_4)_4$, are without question unique and unusual compositions of matter, but analytical data alone do not identify structure and bonding. The several facts reported above indicate strongly that the compounds are true coordinate complex compounds, with the perchlorate anion functioning as a ligand.

Molecular weight data show that $NO_2Al(ClO_4)_4$ exists in solution in sulfur dioxide as the unit $NO_2Al(ClO_4)_4$, with perhaps some tendency to dissociate or ionize in more dilute solutions. This fact indicates that the fourth perchlorate group is bound tightly to aluminum, and the solution process cannot therefore be a co-dissolution of nitronium perchlorate and aluminum perchlorate. The molecular weight in sulfur dioxide of $NH_4Al(ClO_4)_4$ is approximately 60 per cent of the formula weight, or higher than that expected of a solution containing aluminum perchlorate and associated ammonium perchlorate. The data in this case are consistent with essentially complete ionization in accord with the equilibrium process.

$$NH_4Al(ClO_4)_4 \rightleftharpoons NH_4^+ + Al(ClO_4)_4^-$$

The fact that the complex compositions are highly soluble in sulfur dioxide, phosgene and nitromethane is in itself strong evidence of complex formation. As stated previously, ammonium perchlorate and nitronium perchlorate are but slightly soluble in these solvents. This fact surely indicates that ammonium perchlorate and nitronium perchlorate bond readily to aluminum perchlorate. Solubilization by complex formation is also indicated for NH_4ClO_4-$AlCl_3$ and $KClO_4$-$AlCl_3$. One concludes

for both types of complexes that coordinate bonds are formed between ClO_4^- and AlX_3, and that in the $Al(ClO_4)_4$ unit four equivalent Al-$OClO_3$ bonds exist.

X-ray, Raman, and infrared data also serve to indicate the uniqueness of these substances. In the infrared, the antisymmetric ClO_4 stretching mode is split into three components, and the symmetric stretch of free ClO_4^- is observed as a strong, broad band, implying lower symmetry of the complexed ClO_4^- as expected. In the Raman, the antisymmetric bending mode is observed as a doublet at 635 cm^{-1} and 680 cm^{-1}, and the symmetric stretching mode is shifted considerably, from the usual 936 cm^{-1} to 970 cm^{-1}. The infrared data are consistent with reduction in symmetry of the ClO_4^- to C_{2v}, and the Raman data with C_{3v} symmetry. The spectra data can thus be construed as evidence of either monodentate or bidentate coordination, or possibly of both types of coordination. This question can be definitively resolved only by crystallographic studies.

The relative strengths of distortional forces acting on ClO_4^- can qualitatively be deduced from spectral data. The splitting observed by Ross[7] for the antisymmetric stretching mode in ionic perchlorates extended approximately from 1090 cm^{-1} to 1140 cm^{-1}. The antisymmetric bending mode was split about 10 cm^{-1}, from about 625 cm^{-1} to 635 cm^{-1}. These modes were more widely split in $NO_2Al(ClO_4)_4$, the ranges being 1040 cm^{-1} to 1280 cm^{-1} and 635 cm^{-1} to 680 cm^{-1}. This fact, as well as the shift in frequency of the symmetric stretching mode from 936 - 940 cm^{-1} to 970 cm^{-1} in $NO_2Al(ClO_4)_4$ indicates a pronounced reduction in symmetry and the existence of a fairly strong distortional force acting on ClO_4^-. If one assumes that forces responsible for distortion reside in a metal-perchlorate bond, bond strengths are qualitatively comparable to those of anhydrous copper perchlorate[4].

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The spectral data thus are consistent with the proposed coordinate structure, $Al(ClO_4)_4^-$, and they indicate a moderately strong bond between perchlorate and aluminum. One cannot with certainty define more specifically the nature of the bond or the symmetry of the ligand. The authors are of the opinion, however, that bonding is most accurately described by the term partial covalency or by a moderate overlap between orbitals of aluminum and the perchlorate ion. A strong overlap would be conducive to rupture of the Cl-O bond and formation of aluminum oxide. Anhydrous aluminum perchlorate is no doubt unstable for this reason. In the tetra-coordinate complexes the strength of the $Al-OClO_3$ bond is sufficiently strong to insure the integrity of the complex structure, but not strong enough to facilitate oxide extraction. Addition of the fourth perchlorate group apparently results in a slightly weaker bond in the complex than in aluminum perchlorate. The bond weakening effect would be an obvious and natural consequence with electrostatic bonds. With partially covalent bonds, bond weakening is less obvious, but reasonable if bond formation is pictured in terms of fulfilling the needs of the highly electrophilic Al^{+3} ion for electrons. This need can be supplied with a lower average bond energy with four perchlorate ions than with an average of three in aluminum perchlorate.

It is proposed that the mode of formation of the complex perchlorates consists of addition of perchlorate ion to aluminum chloride followed by a stepwise substitution of perchlorate for chloride.

$$ClO_4^- + AlCl_3 \longrightarrow ClO_4AlCl_3^-$$

$$ClO_4AlCl_3^- + 3ClO_4^- \longrightarrow Al(ClO_4)_4^- + 3Cl^-$$

$$AlCl_4^- \longrightarrow AlCl_3ClO_4^- \longrightarrow Al(ClO_4)_4^-$$

Such a mechanism is consistent with general solubility relationships, and avoids the unstable aluminum perchlorate as an intermediate.

ADKNOWLEDGMENT - The support of the Office of Naval Research is gratefully acknowledged.

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III. COMPLEX PERCHLORATES - HEXAPERCHLORATOALUMINATES

C. R. Guibert, J. S. Hashman, H. F. Klodowski and A. D. McElroy

Four complex perchlorates of the type $M_3Al(ClO_4)_6$ (M = NO_2, Li, NH_4 and $(CH_3)_4N$) have been prepared. Efforts to prepare similar derivatives (M = K, N_2H_5, and $C(NH_2)_3$) were unsuccessful. The hexaperchloratoaluminates are substantially more stable than tetraperchloratoaluminates reported previously.[1] Spectroscopic data indicate the perchlorate group to be distorted considerably from the T_d symmetry of the isolated ion, consistent with weak coordinate-covalent bonding, and it is proposed that the compounds contain six perchlorate groups bonded coordinately to a central aluminum atom.

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(1) C. R. Guibert, H. F. Klodowski, M. D. Marshall and A. D. McElroy, "Complex Light Metal Perchlorates" submitted to Inorganic Chemistry.

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INTRODUCTION

The first paper of this series[1] describes the preparation and characterization of $NO_2Al(ClO_4)_4$ and $NH_4Al(ClO_4)_4$. These tetraperchloratoaluminates were stable at ambient temperatures, but decomposed slowly at about 50°C to impure materials exhibiting x-ray diffraction patterns of two new compounds. Other methods described herein yielded the compounds $(NO_2)_3Al(ClO_4)_6$ and $(NH_4)_3Al(ClO_4)_6$, and the x-ray diffraction patterns of these are identical to the patterns of the decomposition products of $NO_2Al(ClO_4)_4$ and $NH_4Al(ClO_4)_4$. Two additional compounds, $Li_3Al(ClO_4)_6$ and $((CH_3)_4N)_3Al(ClO_4)_6$, were also prepared. The hexaperchloratoaluminates are insoluble in solvents which do not displace at least one perchlorate, and thus are more difficult to characterize than the tetraperchloratoaluminates. Available evidence indicates the hexaperchloratoaluminates contain perchlorate bonded in qualitatively the same manner as in the tetraperchlorato complexes. We propose that the $M_3Al(ClO_4)_6$ compounds contain six equivalent perchlorate ions coordinately bonded to a central aluminum ion.

Methods used to prepare the compounds are indicated in Eqs. I through IV:

$$6\ NO_2ClO_4 + AlCl_3 \xrightarrow[-10^\circ]{SO_2} (NO_2)_3Al(ClO_4)_6 + 3\ NO_2Cl \qquad \text{I}$$

$$3\ NO_2ClO_4 + 3\ MClO_4 + AlCl_3 \xrightarrow[-10^\circ]{SO_2} M_3Al(ClO_4)_6 + 3\ NO_2Cl \qquad \text{II}$$

$$(NO_2)_3Al(ClO_4)_6 + AlCl_3 + 6\ NH_4ClO_4 \xrightarrow[vac]{125^\circ} 2(NH_4)_3Al(ClO_4)_6 + 3\ NO_2Cl \qquad \text{III}$$

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$$AlCl_3 \xrightarrow[0^\circ]{N_2O_4} \text{"aluminum nitrate"} + 3\ NOCl \qquad \text{IV a}$$

$$\text{"Aluminum nitrate"} + \text{xs } NO_2ClO_4 \xrightarrow[\text{vac}]{125^\circ} (NO_2)_3Al(ClO_4)_6 + NO_2, \text{ etc} \qquad \text{IV b}$$

$$\text{"Aluminum nitrate"} + \text{xs } NOClO_4 \xrightarrow[\text{vac}]{125^\circ} (NO_2)_3Al(ClO_4)_6 + NO_2, \text{ etc} \qquad \text{IV c}$$

The sulfur dioxide method (Eqs. I and II) is preferred for convenience; 15 to 20 grams of product have been prepared in single experiments, with reaction times of about 4 hours. By-product nitryl chloride is removed along with solvent upon evacuation at ambient temperatures. The method of Eq. III has been used successfully only with the ammonium derivative. The technique represented by Eq. IV is specific for $(NO_2)_3Al(ClO_4)_6$.

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EXPERIMENTAL

Reagents - - Aluminum chloride, nitronium perchlorate, ammonium perchlorate, potassium perchlorate and sulfur dioxide were prepared for use as described in the previous paper[1]. Lithium perchlorate, Fisher-Scientific reagent grade, was dried in vacuo at 110°. Guanidinium perchlorate (K and K) was purified by recrystallization and vacuum drying. Tetramethylammonium and hydrazinium perchlorates were prepared from the chlorides (Eastman Organic Chemicals) by titration in water with silver perchlorate, purified by recrystallization from water and alcohol, and vacuum dried. Dinitrogen tetroxide (Matheson) was treated with oxygen prior to use. Nitromethane (Commercial Solvents Corporation) was distilled (100°, 740 mm) from calcium sulfate, and stored over calcium sulfate.

Preparative reactions in liquid sulfur dioxide - - The procedure generally used is illustrated below for the preparation of $(NO_2)_3Al(ClO_4)_6$. Significant deviations from this procedure are noted in examples of other preparative reactions.

Aluminum chloride (0.311 g) and nitronium perchlorate (2.0157 g) were placed in a round bottom flask which was evacuated and cooled in a dry ice-methanol slurry. Fifteen ml. of sulfur dioxide was distilled into the flask, which was then warmed with stirring to -10°. The slurry was stirred two hours at -10°C, and volatiles were then removed by evacuation on warming to ambient temperatures. The white, crystalline solid (1.696 g, 95.5% yield) was further dried in vacuo at 120°C. Anal. calc'd for $(NO_2)_3Al(ClO_4)_6$: Al, 3.54; N, 5.51; Cl, 27.95. Found: Al, 3.56; N, 5.67; Cl, 27.6; Cl^-, 0.205.

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A 96% yield of $(NH_4)_3Al(ClO_4)_6$ was prepared as above from nitronium perchlorate (2.0 g), ammonium perchlorate (1.6 g) and aluminum chloride (0.63 g). Anal. Calc'd for $(NH_4)_3Al(ClO_4)_6$: Al, 3.98; N, 6.19; Cl, 31.4. Found: Al, 4.0; N, 6.14; Cl, 30.7.

$Li_3Al(ClO_4)_6$ was synthesized by the above procedure from lithium perchlorate, nitronium perchlorate, and aluminum perchlorate. Anal. Calc'd for $Li_3Al(ClO_4)_6$: Al, 4.2; Li, 3.2; Cl, 33.0. Found: Al, 4.18; Li, 3.19; Cl, 32.7. When the same procedure was used with reagents present in the ratio 1 $LiClO_4$: 1 $AlCl_3$: 3 NO_2ClO_4, the low purity product exhibited the x-ray pattern of $Li_3Al(ClO_4)_6$.

To prepare $((CH_3)_4N)_3Al(ClO_4)_6$, aluminum chloride (0.15 g) and tetramethylammonium perchlorate (0.51 g) were premixed in 15 ml of sulfur dioxide at -10°. Nitronium perchlorate (0.51 g) was added via a pistol attached to a side arm. After stirring for 2 hours at -10° the volatiles were removed, and the pale yellow, shock sensitive solid was dried in vacuo at ambient temperatures. Anal. Calc'd for $[(CH_3)_4N]_3Al(ClO_4)_6$: Al, 3.19; C, 17.0; H, 4.25; N, 4.96; Cl, 25.18. Found: Al, 3.16; C, 17.0; H, 4.29; N, 5.0; Cl, 24.2.

Attempts to prepare $K_3Al(ClO_4)_6$ by the technique employed for $(NH_4)_3Al(ClO_4)_6$ yielded products containing potassium perchlorate by x-ray analyses. The method used for $((CH_3)_4N)_3Al(ClO_4)_6$ was employed in an attempt to prepare $(C(NH_2)_3)_3Al(ClO_4)_6$; products exhibited a unique x-ray pattern, but were inexplicably high in carbon and hydrogen contents. Similar attempts to prepare $(N_2H_5)_3Al(ClO_4)_6$ gave products low in $N_2H_5^+$ content.

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Preparation via solid-solid reactions - - "Aluminum nitrate" was prepared from aluminum chloride by reaction overnight at 0° with liquid dinitrogen tetroxide followed by evacuation at ambient temperature until brown fumes no longer evolved. The "aluminum nitrate" produced from aluminum chloridc and dinitrogen tetroxide was a yellow, amorphous solid. Analyses varied from run to run, but ordinarily revealed N and Al to be present in the ratio 4:1. NO^+ or NO_2^- was present in quantities consistent with representation of the "aluminum nitrate" as $AlONO_3$-3 $NOAl(NO_3)_4$. Aluminum nitrate produced from aluminum chloride (3.0 g) was mixed with nitronium perchlorate (24.67 g) in CF_2Cl_2 overnight at -78°C. After removal of CF_2Cl_2, the solids were heated under vacuum, first at 100° for 24 hours and then at 115°C for 24 hours. Solid analyzed - found: N, 5.43; Al, 3.64; Cl, 27.7. Other experiments were identical save that the heating was carried out at 120°-125° for 15-20 hours. A variation of this method consisted of reacting aluminum chloride with dinitrogen tetroxide in the presence of nitronium perchlorate (ca 15 NO_2ClO_4 : $AlCl_3$), followed by heating under a vacuum at 120-125°. The nitronium perchlorate was converted by dinitrogen tetroxide to nitrosonium perchlorate, so that final reacting species were $NOClO_4$ and "aluminum nitrate".

High purity $(NO_2)_3Al(ClO_4)_6$ was produced by these techniques only if an excess of NO_2ClO_4 or $NOClO_4$ was present. Satisfactory ratio's were 9-10 NO_2ClO_4 : $AlCl_3$ and 12-15 $NOClO_4$: $AlCl_3$. Excess reagent was evolved as oxygen and oxides of nitrogen and chlorine.

Attempted preparation of $LiAl(ClO_4)_4$ - - The reaction of aluminum chloride in sulfur dioxide with lithium perchlorate and nitronium perchlorate

(1 $AlCl_3$: 1 $LiClO_4$: 3 NO_2ClO_4), by the technique described in reference 1, yielded impure $Li_3Al(ClO_4)_6$ rather than the desired $LiAl(ClO_4)_4$. One might assume that an initial reaction yielded $LiAl(ClO_4)_4$, which then disproportionated.

$$3\ LiAl(ClO_4)_4 \longrightarrow Li_3Al(ClO_4)_6 + 2\ Al(ClO_4)_3$$

Analyses showed some loss of perchlorate in volatile by-products, and retention of some nitrogen as nitrate in the solid product. The analytical data were consistent with oxynitrates and oxyperchlorates of aluminum as by-products.

Properties of Complex Perchlorates

All the products (pure and impure) are white crystalline powders with unique x-ray diffraction pattern except as noted above. All dissolve readily in water with hydrolysis to appropriate aqueous species. Hydrolysis also occurs on exposure to moist air, eventually with deliquescence. Specific properties are presented below.

Density - - Densities were determined by displacement in Kel-F oil. Values found, in g/cc at 25°C are: $Li_3Al(ClO_4)_6$ - 2.48; $(NO_2)_3Al(ClO_4)_6$ - 2.35; and $(NH_4)_3Al(ClO_4)_6$ - 2.09. The ratio of the density of $(NO_2)_3Al(ClO_4)_6$ to that of $(NH_4)_3Al(ClO_4)_6$ is very nearly equal to the ratio of molecular weights. The density of $Li_3Al(ClO_4)_6$ is higher than that of lithium perchlorate (2.42), and considerably higher than the value reported for aluminum perchlorate[2] (2.20); the high density is not unexpected of a complex comprised of derivatives of two small and highly charged elements.

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(2) Gonzales de Barcia and Moles E., Anales soc. espan, fis quim., 34, 802, (1936).

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Standard Heats of Formation - - These were calculated from measurements of heats of hydrolysis. Values so obtained, in Kcal/mol at 298°K are: $(NO_2)_3Al(ClO_4)_6$, -120±5; $(NH_4)_3Al(ClO_4)_6$, -348±10; and $Li_3Al(ClO_4)_6$, -414±10. These values are self consistent in that the enthalpy changes for the reactions

$$3\ MClO_4 + M'_3Al(ClO_4)_6 \longrightarrow M_3Al(ClO_4)_6 + 3\ M'ClO_4$$

are no more than 5 Kcal for any combination.

Thermal Stability - - No evidence of instability has been observed for any of the compounds, including impure materials, at ambient temperatures. In sealed melting point capillaries, $(NO_2)_3Al(ClO_4)_6$ melted with decomposition at 145-150°C, $(NH_4)_3Al(ClO_4)_6$ appeared to melt at 280-300°C, and $Li_3Al(ClO_4)_6$ did not melt or visibly decompose at temperatures up to 250°C. Differential thermal analyses (10° rise/min., 5 g sample) yielded the following results: $(NO_2)_3Al(ClO_4)_6$ - a small endotherm at 140°-150°C followed by a large exotherm at 170°-230°C; $Li_3Al(ClO_4)_6$ - small exotherms at 100°-115°C and 180°C followed by a large exotherm at 197°C; $(NH_4)_3Al(ClO_4)_6$ - small exotherms at 109°-124°C and 211°-224°C and a moderate exotherm at 232°-257°C. Two samples of $(NH_4)_3Al(ClO_4)_6$ exploded in the DTA apparatus, one at 100°C and the second at about 200°C, while two additional samples yielded traces up to the temperature limit of the apparatus. This unpredictable behavior renders it difficult to specify the temperature limit of the stability of $(NH_4)_3Al(ClO_4)_6$; with small samples it has been our experience that this compound is stable up to about 200°C. At about this temperature both $(NH_4)_3Al(ClO_4)_6$ and $Li_3Al(ClO_4)_6$ begin to decompose at a measurable rate, with ammonium perchlorate and lithium perchlorate being formed in addition to aluminum

oxide. The decomposition thus appears to involve splitting out of one of the parent perchlorates accompanied in effect by decomposition of aluminum perchlorate to chlorine oxides, oxygen and aluminum oxide.

Since $(NO_2)_3Al(ClO_4)_6$ is stable at temperatures at which both parent perchlorates are unstable, decomposition proceeds to aluminum oxide, oxygen and volatile oxides of chlorine and nitrogen. The stability of the compound is such that a temperature of 140°C is required for significant decomposition to occur in a few days time. Periodic analyses of products treated at 140° under vacuum gave results entirely consistent with the decomposition reaction

$$(NO_2)_3Al(ClO_4)_6 \longrightarrow 1/2\ Al_2O_3 + \text{volatiles}.$$

Chlorine and nitrogen were evolved in a ratio of 2Cl : 1N, and the x-ray pattern of the residue remained that of $(NO_2)_3Al(ClO_4)_6$ through better than 50% decomposition.

Hydrolytic Stability - - Samples of $(NO_2)_3Al(ClO_4)_6$, $Li_3Al(ClO_4)_6$ and $(NH_4)_3Al(ClO_4)_6$ were exposed to a 30% relative humidity atmosphere for extended periods of time. The relative gains in weight were approximately the same for the three compounds for two days (3-5%). A steady absorption was observed for $(NH_4)_3Al(ClO_4)_6$ up to a point at which the water content was that required for $3\ NH_4ClO_4 \cdot Al(H_2O)_9(ClO_4)_3$; with $Li_3Al(ClO_4)_6$ water absorption continued past an equivalent point at a steady rate.

Absorption of water vapor was the only net change observed with $(NO_2)_3Al(ClO_4)_6$ for about three days. Thereafter, additional water uptake was

accompanied by loss of nitrogen as nitric acid. After 10 days, volatilization of nitric acid was essentially complete. The point at which nitric acid evolution began corresponds to six moles of water per mole of $(NO_2)_3Al(ClO_4)_6$, or the hydrolysis to 3 HNO_3 - 3 $HClO_4$ - $Al(H_2O)_3(ClO_4)_3$. This suggests that during the initial stages of hydrolysis aluminum competes on equal terms with "nitronium perchlorate", and only after absorption of sufficient water for formation of $Al(H_2O)_3^{+3}$, nitric acid and perchloric acid does incoming water become available for formation of hydronium perchlorate and release of nitric acid.

Reactivity - - Few specific studies have been made of the chemistry of the complex perchlorates. The nitronium derivative is, as might be expected, quite reactive. Ethers and olefins burn spontaneously, for example, and aromatics darken slowly. The lithium and ammonium derivatives are by comparison unreactive; it is recommended however, that indiscriminate contact with organic materials be avoided.

Three reactions of $(NO_2)_3Al(ClO_4)_6$ have been studied in some detail. One of these serves as an alternate method to synthesize $(NH_4)_3Al(ClO_4)_6$. At 100° under vacuum reaction proceeds in accordance with the equation

$$6\ NH_4ClO_4 + AlCl_3 + (NO_2)_3Al(ClO_4)_6 \longrightarrow 2\ (NH_4)_3Al(ClO_4)_6 + 3\ NO_2Cl.$$

This reaction indicates the existence of the NO_2^+ ion in the complex as well as its availability for reactions expected of it.

Liquid dinitrogen tetroxide reacts with $(NO_2)_3Al(ClO_4)_6$ to yield nitrosonium perchlorate and an aluminum nitrate of much the same makeup as

described earlier. This reaction is essentially the reverse of Eq. IV c.

$$x\text{'s } N_2O_4 + (NO_2)_3Al(ClO_4)_6 \longrightarrow 6\ NOClO_4 + \text{"}NOAl(NO_3)_4\text{"}$$

The failure to detect nitronium perchlorate as a product is not unexpected, since it has been observed[3] that nitronium perchlorate is decomposed by dinitrogen tetroxide to nitrosonium perchlorate. The displacement of perchlorate by nitrate can be construed as evidence of the relative coordinating abilities of nitrate and perchlorate, with perchlorate of course appearing to be the weaker of the two. It is suggested however, that this particular displacement is dependent more on the relative stabilities of the product than on comparative coordination strengths. Moreover, the fact remains that, with aluminum, perchlorate is definitely preferred at elevated temperatures, and "aluminum nitrate" is susceptible to decomposition at lower temperatures than $(NO_2)_3Al(ClO_4)_6$.

Nitromethane appears to dissolve $(NO_2)_3Al(ClO_4)_6$ readily. An insoluble residue of nitronium perchlorate is found on filtration of the solution. The quantity of nitronium perchlorate is equal to that shown by the equation

$$(NO_2)_3Al(ClO_4)_6 \longrightarrow (NO_2)_2Al(ClO_4)_5 + NO_2ClO_4$$

Evacuation of the soluble fraction yields first a viscous liquid and eventually a yellowish slightly gummy solid. The analytical data for this solid agreed well with the above reaction scheme in that the Cl:Al ratio was 5:1. Analyses for carbon, hydrogen and nitrogen never satisfactorily resolved the question of the

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(3) Hashman, Marshall, Lewis and McElroy, manuscript in preparation.

extent of solvation of the residue by nitromethane. A reasonable fit with the data was given by the formula $(NO_2(_2Al(ClO_4)_5 \cdot 0.5CH_3NO_2$. This formula is reasonable if one assumes that nitromethane bridges two aluminum atoms to preserve hexacoordinacy. On the other hand, the powder pattern of the solid was that of $(NO_2)_3Al(ClO_4)_6$. It thus is more likely that, as nitromethane was removed, disproportionation of $(NO_2)_2Al(ClO_4)_5$ to $(NO_2)_3Al(ClO_4)_6$ and $NO_2Al(ClO_4)_4$ occurred. The tetracoordinate complex would according to this picture be solvated with one mole of nitromethane.

The same basic reaction (displacement of nitronium perchlorate and formation of highly soluble, highly solvated materials) occurred with $(NO_2)_3$-$Al(Cl\ \ )_6$ and nitroethane or nitropropane. With both nitroalkanes the moles of displ ed nitronium perchlorate was greater than one but never quite two. Removal of solvent yielded gummy untractable materials which proved to be unsafe to handle.

Lithium perchlorate was added to nitromethane solutions of "$(NO_2)_2$-$Al(ClO_4)_5$" in an attempt to displace nitronium perchlorate.

$$2\ LiClO_4 + (NO_2)_2Al(ClO_4)_5 \longrightarrow Li_2Al(ClO_4)_5 + 2\ NO_2ClO_4$$

No displacement occurred, which indicates that "$(NO_2)_2Al(ClO_4)_5$" does not ionize in nitromethane. This is consistent with the observation[1] that $NO_2Al(ClO_4)_4$ does not ionize in liquid sulfur dioxide.

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Infrared and Raman Spectra

Infrared and Raman spectra were obtained by techniques described previously[4]. The data is presented in Table I. The Raman spectrum of nitronium perchlorate[4] and the infrared spectrum of copper (II) perchlorate[5] are included in the table.

TABLE I

SPECTRA OF PERCHLORATES

NO_2ClO_4 (R) R*	$(NO_2)_3Al(ClO_4)_6$ R	$(NO_2)_3Al(ClO_4)_6$ IR	$(NH_4)_3Al(ClO_4)_6$ IR	$Li_3Al(ClO_4)_6$ IR	$Cu(ClO_4)_2$ IR
448 (15)					
471 (20)	485 (19)				
571 (5)					
625 (13)	627 (12)				
640 (11)	670 (4)				665 m
936 (70)	940 sh 970 (47)	920 m	925 m	950 s	920 s
1080 (8)	1110 (8)	1030 s	1040 s	1045 sh	948 s
1095 (8)	1180 (17)	1110 s	1080-1130 m	1060 s	1030 w
1139 (11)	1215 (14)	1180 sb	1180 sb	1165 sh	1130 s
1396 (69)	1398 (36)		1430 s (NH_4^+)	1200 s	1270-1245 sb

* Numbers in parentheses indicate relative intensities.

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(4) J. W. Nebgen, H. F. Klodowski, and A. D. McElroy, "Infrared and Raman Spectra of Nitronium Perchlorate", Inorg. Chem., 4, 1796 (1965).

(5) B. J. Hathaway and A. E. Underhill, J. Chem. Soc. 3091 (1961).

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The symmetric NO_2^+ stretching mode is strongly exhibited in the Raman spectrum of $(NO_2)_3Al(ClO_4)_6$ at 1398 cm^{-1}, but the weak NO_2^+ bend at 570 cm^{-1} observed for NO_2ClO_4[4] is not evident. The remaining absorbances, with the exception of the 1430 cm^{-1} bond for NH_4^+, are due to the ClO_4 group. The symmetric ClO_4^- stretching frequency is medium to strong in the infrared of the complex perchlorates, and is shifted to 970 cm^{-1} in the Raman spectrum of $(NO_2)_3Al(ClO_4)_6$. The antisymmetric ClO_4^- stretching frequency is strongly split in the complex perchlorates; the groups of three infrared absorptions in the 1030-1200 region observed for $(NO_2)_3Al(ClO_4)_6$ and $(NH_4)_3Al(ClO_4)_6$ are consistent with C_{2v} symmetry, while the two strong peaks in this region for $Li_3Al(ClO_4)_6$ indicates C_{3v} symmetry. The Raman lines at 485, 627 at 670 cm^{-1} are indicative of C_{3v} symmetry in $(NO_2)_3Al(ClO_4)_6$, and the Raman data for this compound thus appear to be inconsistent. The spectral data are useful chiefly in that they indicate a normal NO_2^+ ion and a strongly distorted ClO_4 group.

Structure

The previous paper[1] presented evidence which strongly supports representation of $NO_2Al(ClO_4)_4$ and $NH_4Al(ClO_4)_4$ as tetraperchloratoaluminates, or complexes in which four equivalent perchlorate ions are coordinately bonded to aluminum. Bonding between aluminum and perchlorate was envisioned as being moderately covalent in character, as indicated by spectroscopic evidence of a distorted ClO_4 group. We propose that the hexaperchloratoaluminates described in the present paper contain six perchlorate ions similarly bonded to a central aluminum atom in an octahedral configuration.

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Since the hexaperchloratoaluminates are soluble in solvents sufficiently basic (e.g. nitromethane) to solvolyze the complexes, evidence directly related to structure is limited. The spectral data constitutes the most direct of the evidence relevant to structure. Raman and infrared data show normal NO_2^+ and NH_4^+ ions, and perchlorate groups qualitatively distorted from T_d symmetry to an extent equivalent to that observed by Hathaway and Underhill[5] for anhydrous copper (II) perchlorate. The strength of the Al-O-ClO_3 bond is very likely less than that of a covalent Al-O bond, and the bond distance slightly longer.

Less direct support of the proposed structure consists of (1) the insolubility of the hexaperchlorato complexes in SO_2 versus the solubility of the tetra complexes, two moles of $MClO_4$ obviously complex with $MAl(ClO_4)_4$; (2) unique x-ray patterns; (3) the ease of syntheses of high purity material, particularly at elevated temperatures where decomposition to aluminum oxide might be anticipated, and where both NO_2ClO_4 and $NOClO_4$ decompose rapidly; and (4) high stabilities compared to the stabilities of nitronium perchlorate and aluminum perchlorate.

These facts in combination with the more definitive evidence presented for $NH_4Al(ClO_4)_4$ and $NO_2Al(ClO_4)_4$[1] constitute the case for structure at the moment.

The relatively low stability of $NH_4Al(ClO_4)_4$ and $NO_2Al(ClO_4)_4$ and their transformation to $(NH_4)_3Al(ClO_4)_6$ and $(NO_2)_3Al(ClO_4)_6$ show a marked preference for the hexacoordinated configuration. It is likely that aluminum is hexacoordinate, through bridging perchlorate groups, in the tetraperchlorato complexes. A bridged structure would facilitate conversion of $MAl(ClO_4)_4$ to $M_3Al(ClO_4)_6$. We suggest, however, that Al-O bonds are stronger in the tetraperchlorato than in

the hexaperchlorato complexes, and that the conversion is initiated by rupture of Cl-O bonds rather than Al-O bonds.

Reaction Mechanisms

The mechanism of formation of the hexaperchloratoaluminates in sulfur dioxide is believed to be essentially the same as mechanism proposed for tetraperchlorates. The first step consists of formation of a soluble mixed complex:

$$MClO_4 + AlCl_3 \longrightarrow MAlCl_3ClO_4$$

Cloride ion is then successively displaced:

$$3\ NO_2ClO_4 + MAlCl_3ClO_4 \longrightarrow 3\ NO_2Cl + MAl(ClO_4)_4$$

Finally, two moles of perchlorate add, and an insoluble complex precipitates:

$$2\ MClO_4 + MAl(ClO_4)_4 \longrightarrow M_3Al(ClO_4)_6$$

The synthesis of $(NO_2)_3Al(ClO_4)_6$ at elevated temperatures obviously requires a complex overall reaction. The major reaction is clearly Lewis acid-base elimination of nitrate and oxide as follows:

$$NO_2ClO_4 + [AlNO_3] \longrightarrow N_2O_5 + [AlClO_4]$$

$$NOClO_4 + [AlNO_3] \longrightarrow N_2O_4 + [AlClO_4]$$

$$NO_2ClO_4 + [AlO] \longrightarrow [Al(NO_3)(ClO_4)]$$

We propose that the overall mechanism preserves hexacoordinate aluminum at all times through stepwise addition of perchlorate and displacement of nitrate.

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Rosolovski and Rumyantseo[6] report that nitronium perchlorate is a major decomposition product of nitrosonium perchlorate. This fact accounts for the generation of NO_2^+ in the $NOClO_4$ - aluminum nitrate system.

Acknowledgement: This work was supported by the Office of Naval Research and by the Air Force Flight Test Center, Air Research and Development Command, United States Air Force.

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(6) V. Ya. Rosolovski and E. S. Rumyantseo, Russ. J. Inorg. Chem., 8, 689, (1963).

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IV. COMPLEX PERCHLORATES - COMPLEXES OF BORON, BERYLLIUM, ZINC AND TITANIUM

C. R. Guibert, J. S. Hashman, H. F. Klodowski, and A. D. McElroy

The following complex perchlorates have been prepared: $NH_4B(ClO_4)_4$, $NO_2B(ClO_4)_4$, $NO_2Be(ClO_4)_4$, $NO_2Zn(ClO_4)_3$, $LiZn(ClO_4)_3$ and $(NO_2)_2Ti(ClO_4)_6$. These generally were synthesized by reaction of nitronium perchlorate with metal halide, with ammonium perchlorate or lithium perchlorate added as required. Sulfur dioxide, phosgene and nitromethane served as reaction solvents. The derivatives of boron are the least stable of complexes prepared to date, being less stable than $NH_4Al(ClO_4)_4$ and $NO_2Al(ClO_4)_4$. The zinc complexes are the most stable of the group discussed in the present paper.

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INTRODUCTION

In two previous papers[1,2] the syntheses and characterization of tetraperchlorato- and hexaperchloratoaluminates were discussed. The evidence presented for the aluminum complexes was interpreted in terms of coordination of four or six perchlorate ions to the central aluminum atom. The hexaperchloratoaluminates were substantially more stable than the tetraperchloratoaluminates, as evidenced by slow decomposition of the latter at 50°C, and by rearrangement to the six-coordinate complexes. Evidence relevant to bonding showed that the perchlorate group is considerably distorted from a regular tetrahedral configuration, and this was interpreted to mean that bonding was partially covalent, though the nature of bonding is far from being adequately defined.

In this paper we shall present results of successful efforts to prepare complex perchlorates of other central elements, namely boron, beryllium, zinc and titanium.

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(1) C. R. Guibert, H. F. Klodowski, M. D. Marshall and A. D. McElroy, Complex Light Metal Perchlorates, Submitted to Inorganic Chemistry.
(2) C. R. Guibert, J. S. Hashman, H. F. Klodowski and A. D. McElroy, Complex Perchlorates II, Hexaperchloratoaluminates.

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EXPERIMENTAL

Reagents - - A majority of the reagents are described in preceding papers[1,2]. Boron trichloride was purified by vacuum line fractionation through a trap held at dry ice - methanol slush bath temperature. Phosgene (Matheson) was treated with nitronium perchlorate, and that fraction which passed through a dry ice-methanol trap and stopped at -111° (CCl_3F slush) was used as a reaction solvent. Fisher Scientific titanium tetrachloride was fractionally distilled (collected at -23° after passing through 0°) under vacuum. Anhydrous zinc chloride was prepared by dehydration of the hydrate (Fisher Scientific) with thionyl chloride at reflux temperature. Beryllium chloride (Chemical Products Laboratory) was vacuum sublimed at 300°C.

$(NO_2)_2Be(ClO_4)_4$ - - This compound dissolved readily in liquid sulfur dioxide. The preparative scheme consisted of reaction of an excess of nitronium perchlorate with beryllium chloride in sulfur dioxide at -10°, followed by filtration and evaporation of volatile from the filtrate

$$4\ NO_2ClO_4 + BeCl_2 \longrightarrow (NO_2)_2Be(ClO_4)_4 + 2\ NO_2Cl$$

Anal. calc'd. for $(NO_2)_2Be(ClO_4)_4$: Be, 1.78; N, 5.62; Cl, 28.3. Found: Be, 1.79; N, 5.60; Cl, 26.7. ΔH°_f = -70± 6 kcal/mol; d = 2.17-2.20 g/cc.

Several attempts to prepare $(NH_4)_2Be(ClO_4)_4$ and $Li_2Be(ClO_4)_4$ were unsuccessful. Typical reaction systems are as follows: 2 NO_2ClO_4 - 2 NH_4ClO_4 - $BeCl_2$ in SO_2; 2 NH_4Cl - 4NO_2ClO_4 - $BeCl_2$ in SO_2; 2 NH_4Cl - 4 $AgClO_4$ - $BeCl_2$ in SO_2, and 2 NH_4Cl - $(NO_2)_2Be(ClO_4)_4$ in SO_2. In no instance was a product of

satisfactory purity obtained. X-ray diffraction patterns indicated unreacted lithium perchlorate or ammonium perchlorate, as well as $(NO_2)_2Be(ClO_4)_4$ in reactions involving NO_2ClO_4 or $(NO_2)_2Be(ClO_4)_4$.

Under conditions favoring a complex of the type $MBe(ClO_4)_3$, where M = Li or NH_4, liquid, sulfur dioxide-soluble, products were obtained. These analyzed poorly for $MBe(ClO_4)_3$, with assumption of oxide formation being necessary. It has tentatively been concluded that Be-O-Be bonds are responsible for the liquid, probably polymeric, character of these products.

$(NO_2)_2Ti(ClO_4)_6$ - - Titanium tetrachloride reacts readily with nitronium perchlorate in phosgene, sulfur dioxide, and in the absence of a solvent. The reaction is in fact apparently too spontaneous, as it was difficult to obtain products free of NO^+ or NO_2^-, and of excess nitrogen, apparently as NO_3^-. Products varying considerably in purity exhibited identical X-ray patterns, which did not show $NOClO_4$ or NO_2ClO_4 to be present. The best procedure consisted of extended reaction times at dry ice temperature in liquid phosgene

$$6\ NO_2ClO_4 + TiCl_4 \longrightarrow (NO_2)_2Ti(ClO_4)_6 + 4\ NO_2Cl$$

Titanium tetrachloride (0.43 g) was distilled into an evacuated two neck round bottom flask immersed in liquid nitrogen. Phosgene (approx. 15 ml) was distilled into the flask and a pistol containing nitronium perchlorate (1.98 g) was attached while sweeping the flask with nitrogen. The flask was again evacuated, the nitronium perchlorate added, and the mixture warmed to -78°C by replacing the liquid nitrogen with a dry ice-methanol slush bath. A white cloudy solution formed upon warming. The solution stirred overnight

(18 hours) at -78°C changed to a clear but lightly yellow liquid. The apparatus was inverted and the liquid filtered through a medium frit into a receiver cooled to -78°C. Volatile materials were distilled off under vacuum at -50°C. The white solid extract (1.61 g, 96% yield) was dried in vacuo at room temperature. Anal. Calc'd. for $(NO_2)_2Ti(ClO_4)_6$: N, 3.79; Ti, 6.51; Cl, 28.90. Found: N, 4.62; Ti, 6.57; Cl, 28.2; NO^+, 0.16 meq/g; Cl^-, none. These analyses can be expressed as $(NO^+)_{0.12}\ (NO_2^+)_{1.98}\ Ti(ClO_4)_{5.79}\ (NO_3)_{0.31}$. The chief source of contamination would appear to be due to coordination of nitrate ion in place of perchlorate ion.

$NH_4B(ClO_4)_4$ - - Boron trichloride (1.00 g by PVT) was distilled into an evacuated flask containing ammonium chloride (0.47 g) and nitronium perchlorate (5.00 g). Approximately 20 ml of phosgene was condensed in at -196°C. The flask was then immersed in a dry ice-methanol slush bath and the contents agitated with a magnetic stirrer. In 15 minutes the solution was clear. After four hours the solution was filtered, yielding 0.4 g of a light yellow residue. Evaporation of the filtrate gave 2.64 g (72% yield) of a yellow solid product. Anal. calc'd. for $NH_4B(ClO_4)_4$: B, 2.53; N, 3.27; Cl, 33.2. Found: B, 2.78; N, 3.34; Cl, 32.1. ΔH_f° = -145 ± 9 Kcal/mole. d = 2.15 g/cc.

$(NO_2)\ B(ClO_4)_4$ - - The technique described above works equally well for $(NO_2)\ B(ClO_4)_4$. The nitronium derivative is soluble in phosgene, and filtered solutions yielded the complex in good purity. A second preparative procedure consists of reaction of boron trichloride with nitronium perchlorate (1 BCl_3 : 4 NO_2ClO_4) at -50°. The complex is shock sensitive (47.5 kg cm, 50% test) and the standard heat of formation, ΔH_f = -80 ± 10 kcal/mole. Density is 2.26 g/cc.

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$NO_2Zn(ClO_4)_3$ - - Zinc chloride was found to be considerably less reactive with nitronium perchlorate than are the chlorides of aluminum, boron, beryllium and titanium. Very little reaction occurs in sulfur dioxide, since zinc chloride is negligibly soluble in this solvent. The method used to prepare $NO_2Zn(ClO_4)_3$ consists of intimately mixing an excess of nitronium perchlorate with zinc chloride in sulfur dioxide at -10°C, followed by removal of solvent and heating at 125° under vacuum for 5-10 hours. No evidence of $(NO_2)_2Zn(ClO_4)_4$ was found, and X-ray patterns of charges which had been insufficiently heated showed the presence of NO_2ClO_4 and $NO_2Zn(ClO_4)_3$. Extended heating at 125° yielded $Zn(ClO_4)_2$ contaminated slightly by nitrate and chloride ions.

Zinc chloride (1.66 g) and nitronium perchlorate (10.6 g) were stirred together in liquid sulfur dioxide (15 ml) for two hours. The solvent was removed, and the solids were heated under vacuum at 125°C for 7 hours: yield of final product was 4.8 g (96%). Anal. calc'd. for $NO_2Zn(ClO_4)_3$: N, 3.41; Zn, 15.6; Cl, 25.98. Found: N, 3.38; Zn, 15.8; Cl, 25.85. Heating the compound at 125°C for 7 days yielded a sublimate of nitronium perchlorate and a brown solid which analyzed well for zinc perchlorate. Anal. calc'd. for $Zn(ClO_4)_2$: Zn, 24.73; Cl, 26.83. Found: Zn, 25.76; Cl, 26.34; N, 0.25; Cl^-, 0.67.

Some properties of $NO_2Zn(ClO_4)_3$ are: white, non-shock sensitive; density, 2.7 g/cc; ΔH_f° -48 ± 4 kcal/mol; soluble in nitromethane, insoluble in phosgene and sulfur dioxide.

$LiZn(ClO_4)_3$ - - Sulfur dioxide and phosgene are unsuitable solvents, but nitromethane has been used successfully, however. A second successful method

utilizes solid-solid reactions. The preparative reactions are essentially the same for both methods.

$$LiClO_4 + 2\ NO_2ClO_4 + ZnCl_2 \longrightarrow LiZn(ClO_4)_3 + 2\ NO_2Cl$$

Though elimination of chloride is complete in nitromethane, the product is solvated and must be heated under vacuum. In practice, therefore, an excess of nitronium perchlorate is employed with both methods, with the excess being removed by decomposition under vacuum at 125°C. In one five gram experiment, with nitromethane, the product prior to heating was a tacky solid which exploded and burned during an attempt to remove it from the flask. One to two gram runs were accomplished without incident.

The solid-solid reaction requires about one week at reaction temperature to effect completion. Though the method is tedious, it is preferred to the nitromethane procedure from a safety standpoint. The formation of $NO_2Zn(ClO_4)_3$, in quantity sufficient to be strongly evident by X-ray analysis is believed to result in the slow reaction exhibited by the solid-solid reaction; this compound decomposes very slowly to zinc perchlorate at reaction temperature, and lithium perchlorate is apparently not capable of hastening the displacement process. By this view the reaction mechanism consists of the formation of $NO_2Zn(ClO_4)_3$ followed by decomposition to zinc perchlorate and addition of lithium perchlorate. It is reasonable then to expect addition of other metal perchlorates to zinc perchlorate at elevated temperatures.

Lithium perchlorate (1.58 g), nitronium perchlorate (2.36 g) and zinc chloride (.74 g) were mixed in sulfur dioxide (20 ml) for 2 hours. After evaporation

of the volatiles, the solids were heated to 125°C for 5 days to produce $LiZn(ClO_4)_3$ (1.9 g, 95% yield). It was also prepared by mixing the components (identical weights) in nitromethane at room temperature for 18 hours. A clear yellow solution was obtained. The volatiles were evaporated, the solids washed three times with freon 113 (CCl_2F-$CClF_2$), dried at room temperature overnight, and heated under vacuum at 125°C overnight. No traces of nitromethane were found in the yellow crystalline solid. Anal. calc'd. for $LiZn(ClO_4)_3$: Li, 1.87; Zn, 17.64; Cl, 28.76. Found: Li, 1.87; Zn, 17.2; Cl, 28.4. The compound has a density of 2.78-2.85 gm/cc; ΔH_f° -148 ± 4 kcal/mole; soluble in nitromethane, insoluble in sulfur dioxide and phosgene; and is not shock sensitive.

Attempted Preparation of Chromium and Silicon Derivatives - - Desired products, $(NO_2)_3Cr(ClO_4)_6$ and $(NO_2)_2Si(ClO_4)_6$, were not achieved with either element. Chromium (III) chloride was totally unreactive toward nitronium perchlorate, even at elevated temperatures. Silicon tetrachloride was unreactive at room temperature or at -10°C in sulfur dioxide; reaction occurred in the absence of solvent at elevated temperatures (100-120°C) and in nitromethane at 25°C, but silicon dioxide was the major product. Efforts to dehydrate chromium(III) nitrate and to then effect reaction with nitronium perchlorate were also unsuccessful. In one instance a brown, highly shock sensitive, grossly impure product was obtained; in another instance the reaction proper exploded.

Spectral data have been obtained for $NO_2Zn(ClO_4)_3$, $LiZn(ClO_4)_3$, and $(NO_2)_2Be(ClO_4)_4$. The Raman spectrum of $NO_2Be(ClO_4)_4$ exhibited only two lines--the non-degenerate stretching vibration for ClO_4^- at 945 cm^{-1}, and the NO_2^+ symmetric stretching vibration at 1400 cm^{-1}. Both Raman lines were weak compared

to intensities observed with other compounds. Eight lines, at 450, 480, 615, 670, 960, 1130, 1200, and 1400 cm^{-1} were observed in the Raman spectrum of $NO_2Zn(ClO_4)_3$. Resolution of the symmetric ClO_4^- bending vibration into two lines at 450 and 480 cm^{-1} indicates C_{2v} symmetry, though the doublets at 615-670 cm^{-1} (antisymmetric ClO_4^- bend) and at 1130-1200 cm^{-1} (antisymmetric ClO_4^- stretch) are typical of C_{3v} symmetry[3]. C_{3v} symmetry for the ClO_4 group is indicated by the infrared spectra of $LiZn(ClO_4)_3$ and $NO_2Zn(ClO_4)_3$. Well-resolved groups of three vibrations were observed at 1210 cm^{-1}, 1135 cm^{-1} and 1030 cm^{-1} with $NO_2Zn(ClO_4)_3$, and at 1180 cm^{-1}, 1110 cm^{-1}, and 1040 cm^{-1} with $LiZn(ClO_4)_3$. The infrared-inactive symmetric stretching vibration was observed as weak to moderate bands at 955 cm^{-1} with $NO_2Zn(ClO_4)_3$ and 960 cm^{-1} with $LiZn(ClO_4)_3$.

Solubilities - - Sulfur dioxide readily solubilizes $NH_4B(ClO_4)_4$, $NO_2B(ClO_4)_4$, $(NO_2)_2Be(ClO_4)_4$ and $(NO_2)_2Ti(ClO_4)_6$. This group of compounds also is soluble in phosgene, with the possible exception of $(NO_2)_2Be(ClO_4)_4$, which was not tested. The two zinc complexes are insoluble in sulfur dioxide and phosgene, but are soluble in nitromethane.

Stability - - At ambient temperatures $NO_2B(ClO_4)_4$ and $NH_4B(ClO_4)_4$ change from white to yellow soon after synthesis, and measurable decomposition occurs in 3-4 weeks. Decomposition becomes rapid at 70°-80°C. Ammonium perchlorate and nitronium perchlorate are observed decomposition products. $(NO_2)_2Be(ClO_4)_4$ and $(NO_2)_2Ti(ClO_4)_6$ appear to be stable indefinitely at ambient temperatures. At 90°-100°, both compounds decompose at rates of 5-10%/hour. $NO_2Zn(ClO_4)_3$ decomposes

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(3) B. J. Hathaway and A. E. Underhill, J. Chem. Soc., 3091, (1961).

very slowly at 125°, and melts with decomposition at 160°. The stability of $LiZn(ClO_4)_3$ is higher than that of $NO_2Zn(ClO_4)_3$.

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DISCUSSION

The property of greatest fundamental interest for the group of compounds disclosed in this and previous papers[1,2] is structure and nature of bonding. Are they indeed new and unique members of the coordination family of compounds? Does the perchlorate ion function as a ligand having the ability to bond strongly enough to central metallic elements to insure the integrity and stability of molecular or ionic species typified by $B(ClO_4)_4^-$? The first paper of this series[1] presented evidence gathered in recent years[3,4,5,6,7] which indicate that the perchlorate ion is significantly distorted in a surprising number of compounds. The reduced symmetry has variously been interpreted in terms of monodentate or bidentate ligancy. The only indisputable evidence of ligand character, and thus of at least weak covalent bonding, has been disclosed by Cotton and Weaver[6], who demonstrated this fact through an analysis of structure by the X-ray method.

The evidence relevant to structure for the group of compounds disclosed in this paper is, in addition to analytical data and uniformly unique X-ray diffraction patterns, as follows. The perchlorate group is shown by infrared and Raman studies to be reduced considerably in symmetry relative to isolated ClO_4^-, and is under distortional influences similar to those observed by Cotton and Weaver[6], Hathaway and Underhill[3], and Wickenden and Krause[4]. The present group

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(4) A. E. Wickenden and R. A. Krause, Inorg. Chem., 4, 404, (1965).
(5) S. D. Ross, Spectrochimica Acta, 18, 225, (1962).
(6) F. A. Cotton and D. L. Weaver, J. Am. Chem. Soc., 87, 4189 (1965).
(7) J. W. Nebgen, A. D. McElroy, and H. F. Klodowski, Inorg. Chem., 4, 1796, (1965).

of compounds are quite soluble in one or more non-aqueous solvents, solvents in which the parent $MClO_4$ is insoluble (an exception is $LiZn(ClO_4)_3$, which was soluble only in nitromethane, in which lithium perchlorate is soluble). The solubilization, in effect, of NO_2ClO_4 by $B(ClO_4)_3$ and of NO_2ClO_4 by $Ti(ClO_4)_4$, for example, surely is indicative of complex formation. In the first paper of this series[1], complex formation was substantiated by measurement of the molecular weights of $NH_4Al(ClO_4)_4$ and $NO_2Al(ClO_4)_4$ in liquid sulfur dioxide.

The most convincing arguments for complex formation are the existence, the stability, and the ease of synthesis of complex perchlorates of elements for which simple perchlorates, e.g. $B(ClO_4)_3$, are unknown, very unstable, or of doubtful authenticity. This argument is applicable particularly to perchlorates of boron, aluminum and titanium. Addition of one or more perchlorate ions to the simple perchlorates obviously results in configurations more stable than are possible without complex formation.

Finally, the relative stabilities of the complex perchlorates are consistent with expectations based on properties of the central element and on the number of ClO_4^- ions involved in the complexes. The order of increasing stability is approximately as follows: $NH_4B(ClO_4)_4 \approx NO_2BClO_4 < NH_4Al(ClO_4)_4 \approx NO_2Al(ClO_4)_4 < (NO_2)_2Be(ClO_4)_4 \approx (NO_2)_2Ti(ClO_4)_6 < NO_2Zn(ClO_4)_3 \approx (NO_2)_3Al(ClO_4)_6 < LiZn(ClO_4)_3 \approx (NH_4)_3Al(ClO_4)_6 \approx Li_3Al(ClO_4)_6$. The stabilities generally are lower with the smaller, highly charged central elements, and are increased by addition of more than one perchlorate ion to the parent perchlorate [$Al(ClO_4)_4^-$ vs $Al(ClO_4)_6^{-3}$].

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We prefer not to speculate about or hypothesize specific structural or crystal configurations. It is apparent that all the complexes are consistent with known derivatives of the central elements (BX_4^-, AlX_4^-, AlX_6^{-3}, ZnX_3^- etc). Further study, particularly by the X-ray method, is necessary to define structures. In this connection the question of monodentate or bidentate perchlorate is of particular interest. Spectroscopic data very clearly show the symmetry (C_{2v}) expected of bidentate ClO_4 in some cases, but we are not convinced that this fact indicates two oxygen atoms of ClO_4 to be involved in bonding. This conviction is augmented by the fact that bidentate symmetry is indicated for the hexaperchlorato-aluminates[2], nitronium perchlorate[7], and potassium perchlorate[5].

Since many of the routes to preparation of complex perchlorates involved nitronium perchlorate as a reactant, a considerable amount of experience has been accumulated about the manner of reaction of nitronium perchlorate with metal halides. One aspect of this reaction chemistry is worthy of particular note.

The perchlorate anion of nitronium perchlorate is usually stable or resistant to degradation during reaction with metal halides, even though complicating side reactions involving the nitronium ion take place. The nitronium ion has been observed to react in one or both of two ways. The first involves simple displacement of halide as nitryl chloride:

$$NO_2^+ + Cl^- \longrightarrow NO_2Cl$$

The second consists of a redox reaction illustrated generally by:

$$NO_2^+ + 2\,e^- \longrightarrow NO^+ + O^=$$

or, for illustrative purposes

$$NO_2^+ + BCl_3 \longrightarrow NO^+ + [BOCl] + Cl_2 .$$

The redox mode of reaction was particularly evident with titanium tetrachloride and boron trichloride, and generally occurred in reactions of too great a spontaneity. Furthermore the redox mode was invariably observed as a competitive reaction when reaction stoichiometry was not proper for formation of the appropriate complex perchlorate. For example, in several experiments nitronium perchlorate was reacted with boron trichloride in CF_2Cl_2 in an effort to prepare boron perchlorate:

$$3\ NO_2ClO_4 + BCl_3 \longrightarrow B(ClO_4)_3 + 3\ NO_2Cl$$

In all instances elimination of chloride was essentially quantitative, and perchlorate was quantitatively retained in solid products. These products could be represented fairly consistently by $(NO_x)_2B(ClO_4)_3$. X-ray diffraction patterns usually indicated $NOClO_4$ to be present, and in two instances $NO_2B(ClO_4)_4$ was also found to be present. These results are consistent with the following reaction:

$$6\ NO_2ClO_4 + 2\ BCl_3 \longrightarrow NO_2B(ClO_4)_4 + 2\ NOClO_4 + BONO_3 + 2\ Cl_2 + 2\ NO_2Cl$$

It should be emphasized that the depicted product distribution has been substantiated only qualitatively. Nevertheless, the equation illustrates satisfactorily the types of products to be expected if reactions are not properly moderated, or if reactants are not present in proportions required for synthesis of the stable complex perchlorates.

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V. SYNTHESIS OF THE TETRANITRATOBORATE ANION

C. R. Guibert and M. D. Marshall

The simple nitrate of boron has never been isolated despite efforts by several investigators[1-3]. The products of the reactions are invariably B_2O_3 or possibly $BONO_3$. We wish to report the synthesis of tetramethylammonium tetranitratoborate, $[Me_4N][B(NO_3)_4]$, from the action of liquid dinitrogen tetroxide on the corresponding tetrachloride. The complex has proven to be remarkably stable and possesses rather unexpected properties.

The synthesis was accomplished by adding dinitrogen tetroxide to solid $[Me_4N][BCl_4]$ at -78° (mole ratio $N_2O_4/BCl_4^- > 8:1$); the system was then allowed to warm to 0° over a period of approximately 2 hr. The removal of the excess dinitrogen tetroxide, along with the nitrosyl chloride produced in the reaction, was effected at room temperature, leaving a white, crystalline solid with the approximate composition for the desired product. Prolonged contact with dinitrogen tetroxide, or carrying out the reaction at room temperature, increased the oxynitrate or boric oxide content. Extraction with ammonia removed the complex nitrate, leaving the oxide behind. The solid recovered from the filtrate was analyzed. Anal. Calcd for $[Me_4N][B(NO_3)_4]$: C, 14.41; H, 3.69; B, 3.30; Me_4N^+, 22.22; N (Devarda), 16.81. Found: C, 14.6; H, 4.8; B, 3.32; Me_4N^+, 22.42; N (Devarda), 16.94[4].

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(1) M. Schmeisser, Angew. Chem., 67, 483 (1955).
(2) M. Schmeisser and K. Brandle, ibid., 73, 388 (1961).
(3) D. Lutzow, Dissertation, Munich, 1955.
(4) The total nitrogen by the Dumas method was 19.6% vs. the theoretical value of 21.02%. It has been our experience, however, with tetramethylammonium compounds and complex nitrates in general, that values slightly lower than theoretical are to be expected. The nitrogen balance obtained by adding Devarda (NO_3^-) and tetramethylammonium analyses was 21.18%, or nearly theoretical (21.02%).

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The X-ray powder pattern of the solid was obtained by using Cu Kα radiation and is shown in Table I. The pattern shows no reflections for tetramethylammonium nitrate, a likely impurity.

TABLE I

d, A	RI[a]	d, A	RI	d, A	RI
7.25	s	3.39	s	2.35	w
5.70	m	3.29	w	2.32	w
5.15	s	3.19	w	2.20	vw
4.90	vw	3.15	w	2.15	vw
4.70	vw	3.05	m	2.02	w
4.40	m	2.82	w	1.98	w
3.90	vw	2.64	w	1.94	w
3.80	vs	2.60	w	1.91	w
3.60	w	2.49	w	1.88	w
3.45	w	2.45	w		

a) Relative intensity.

The infrared spectrum in Nujol and KBr shows lines at 669, 743, 755, 767, 887, 950, 1007, 1297, 1311, 1356, 1385, 1416, 1489, 1582, 1612, and 1626 cm^{-1}. The absorptions for ν_4 at 1582 to 1626 cm^{-1} and for ν_1 at 1297 and 1311 cm^{-1} are the two prominent bands. The 1582- and 1626-cm^{-1} lines appear as shoulders on the 1612-cm^{-1} lines. This splitting of the ν_4 and ν_1 absorptions together with the (ν_4-ν_1) separation of 271 to 339 cm^{-1} are expected for unidentate nitrato bonding[5,6]. Ionic nitrate vibrations at $\sim$ 1330 cm^{-1} for tetramethylammonium nitrate were absent from the spectrum.

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(5) K. W. Bagnell, D. Brown, and J. G. H. duPreez, J. Chem. Soc., 5523 (1964).
(6) B. O. Field and C. J. Hardy, Quart. Rev. (London), 18, 385 (1964).

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Molecular weight determinations in acetonitrile in a concentration range of 0.045 to 0.288 M gave a value of 185 ± 15. The theory for $[Me_4N][B(NO_3)_4]$, assuming complete dissociation into two ions, is 166.5. Conductance measurements support dissociation. Equivalent conductance values obtained in acetonitrile at 18° are listed in Table II. A plot of Λ against the square

TABLE II

Concn[a]	Λ[b]	Concn	Λ
0.123	135	0.012	157
0.06	132	0.006	170
0.024	157	0.0024	184

a) Molal, b) In ohm^{-1} cm^{-2}.

root of the concentration is linear and extrapolates to an equivalent conductance of 210 ohm^{-1} cm^{-2} at infinite dilution. Berns and Fuoss[7] report an equivalent conductance for $[Me_4N]NO_3$ in acetonitrile at 25° of 200.5 ohm^{-1} cm^{-2} at infinite dilution. Thus dissociation into two ions is clearly indicated. If the conductivity data are used to calculate the measured molecular weight in the concentration range indicated, a value of about 205 is obtained which checks well with the measured value of 185 ± 15. A preliminary ^{11}B nmr spectrum shows the single expected peak with a chemical shift value of 44.0 ppm relative to $NaBH_4$ in acetonitrile. If the δ value for $NaBH_4$ in acetonitrile is comparable to its value in H_2O, $[Me_4N][B(NO_3)_4]$ has a chemical shift value comparable to $NaB(C_6H_5)_4$ and $NaB(OMe)_4$.

(7) D. S. Berns and R. M. Fuoss, J. Am. Chem. Soc., 83, 1321 (1961).

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The complex is not noticeably soluble in, nor hydrolyzed by cold water. Some solubility is indicated in hot water. It is readily soluble in methanol, acetonitrile, ammonia, and dimethylformamide from which it can be recovered unchanged. Reaction occurs with sulfur dioxide to give products as yet unknown. As mentioned previously, a slow reaction occurs in dinitrogen tetroxide producing the boron oxide linkage.

$[Me_4N][B(NO_3)_4]$ is stable at room temperature; samples have been stored for periods of more than 2 months without noticeable decomposition. The compound is insensitive to shock when struck sharply with a hammer.

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APPENDIX

Synthesis of Complex Nitratoaluminate Anions

Although anhydrous aluminum nitrate has been isolated from the reaction of aluminum chloride with chlorine nitrate[1], complex nitratoaluminates have not been reported. We wish to report the synthesis of tris(tetramethylammonium) hexanitratoaluminate $[Me_4N]_3[Al(NO_3)_6]$ from the action of liquid dinitrogen tetroxide on the mixture of tetramethyl ammonium nitrate and the corresponding tetrachloride. Tetramethylammonium tetranitratoaluminate $[Me_4N][AlNO_3)_4]$ was also obtained through high temperature degradation of the hexanitrato complex, and prolonged contact of the latter with N_2O_4.

The synthesis of the new compound $[Me_4N]_3[Al(NO_3)_6]$ was accomplished by adding excess dinitrogen tetroxide to a 2:1 mixture of Me_4NNO_3 and solid $[Me_4N][AlCl_4]$ at -78°C; the system was then warmed to ambient temperatures for approximately one hour. The reaction occurs as follows:

$$2\ Me_4NNO_3 + [Me_4N][AlCl_4] + X's\ N_2O_4 \longrightarrow [Me_4N]_3[Al(NO_3)_6] + 4\ NOCl$$

The excess dinitrogen tetroxide and the nitrosyl chloride produced were removed by evaporation at room temperature using oxygen as a carrier gas. A white crystalline solid residue when dried at 75°C proved to be the new compound in high purity. The solid recovered from the heat treatment at 75°C analyzed: Anal. calculated for $[Me_4N]_3[Al(NO_3)_6]$: C, 23.19%; H, 5.84%; Me_4N^+, 35.79%; Al, 4.34%;

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(1) M. Schmeisser and K. Brandle, Angew. Chem., 73, 388 (1961).

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N (Dumas), 20.29%; N (Devarda),[2] 13.52%. Found: C, 23.89%; H, 6.31%; Me_4N^+, 35.88%; Al, 4.34%; N (Dumas), 19.19%; N (Devarda), 13.35%.

The X-ray powder of the solid was obtained by using Cu Kα radiation and is shown in Table I. The pattern shows no reflection for tetramethylammonium nitrate, a likely impurity.

TABLE I

d,A	RI[a]	d,A	RI[a]	d,A	RI[a]
6.50	m	3.80	vw	2.62	m
4.90	m	3.60	s	2.42	w
4.60	w	3.40	s	2.20	w
4.40	s	3.03	s	2.00	m
4.00	vs	2.80	ms		

a) Relative Intensity

The infrared spectrum of the powder on NaCl, BaF_2, and Irtran crystals and in Nujol show absorptions at 705, 747, 764, 798, 818, 955, 1015, 1032, 1300, 1340, 1495, 1540, 1590 and 1610 cm^{-1}. The spectrum in Nujol is shown as (a) in Figure I.

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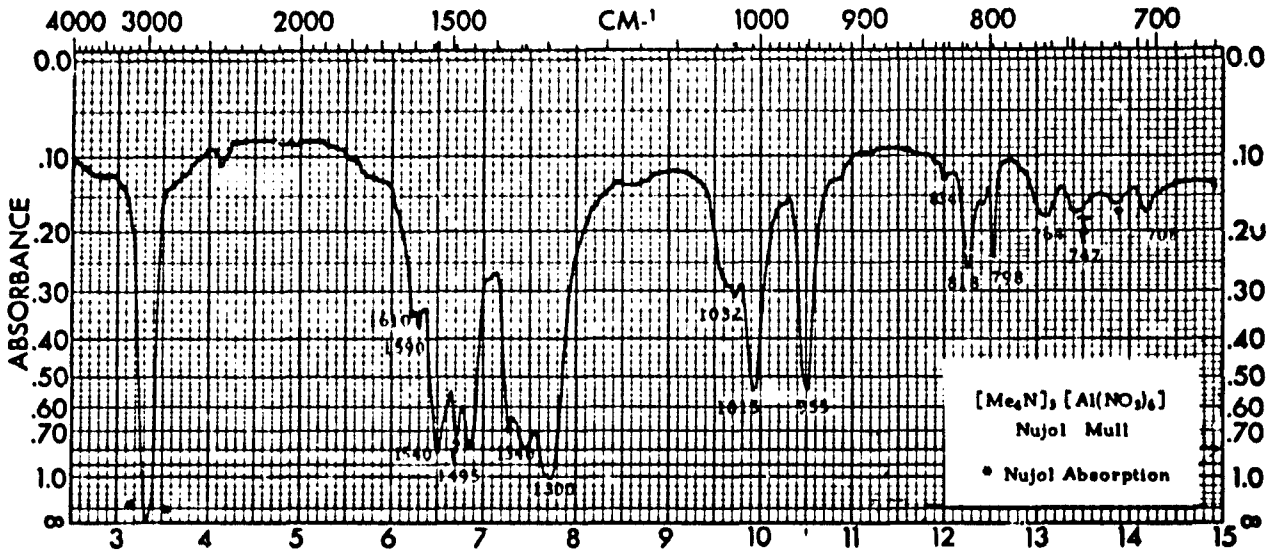
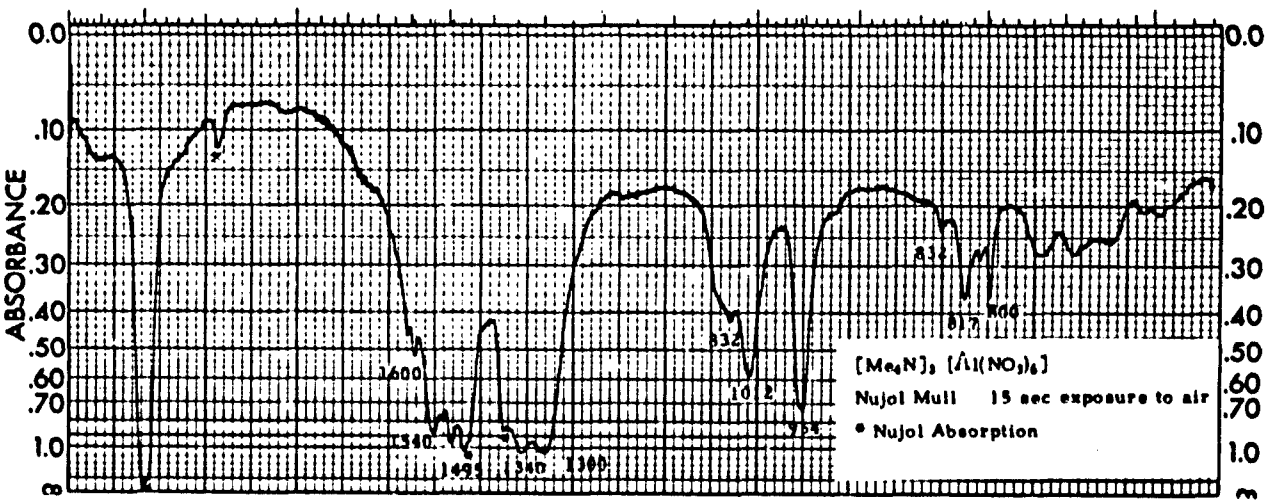
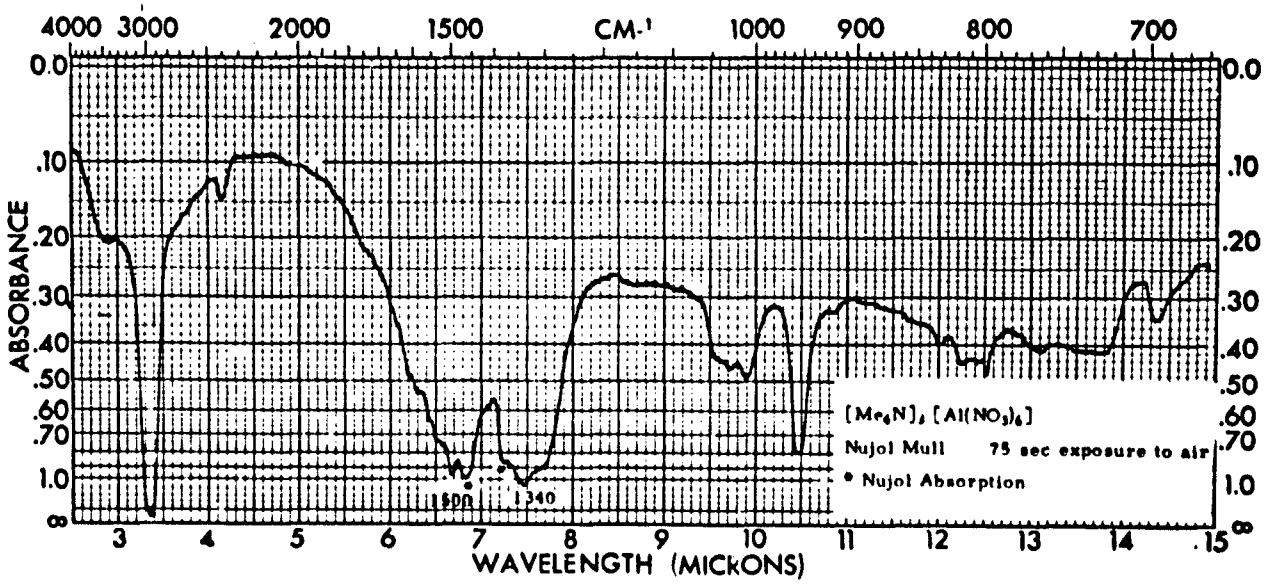
(2) The total nitrogen by the Dumas method was 19.19% vs the theoretical value 20.29%. It has been our experience that nitrogen values determined by the Dumas method for Me_4N^+ compounds and complexes containing NO species slightly lower than theoretical are to be expected. The nitrogen balance obtained by adding Devarda (NO_3^-) and Me_4N^+ analyses was 20.13% or nearly theoretical 20.29%.

FIGURE I


4000 3000 2000 1500 CM-1 1000 900 800 700
ABSORBANCE
0.0 .10 .20 .30 .40 .50 .60 .70 1.0 ∞
1590
1495
1300
1032
1015
959
798
[Me4N]3 [Al(NO3)6]
Nujol Mull
* Nujol Absorption
3 4 5 6 7 8 9 10 11 12 13 14 15


ABSORBANCE
0.0 .10 .20 .30 .40 .50 .60 .70 1.0 ∞
1600
1495
1340
1300
832
1012
959
817
800
[Me4N]3 [Al(NO3)6]
Nujol Mull 15 sec exposure to air
* Nujol Absorption


4000 3000 2000 1500 CM-1 1000 900 800 700
ABSORBANCE
0.0 .10 .20 .30 .40 .50 .60 .70 1.0 ∞
1500
1340
[Me4N]3 [Al(NO3)6]
Nujol Mull 75 sec exposure to air
* Nujol Absorption
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

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Both ionic nitrate and nitrato-type absorptions are present in the spectrum between 1300 and 1610 cm^{-1}. Nitrato-type bands are present at 1300 and 1540 to 1610 cm^{-1}. The nitrate ion, with D_{3h} symmetry, has two doubly degenerate, infrared active, fundamentals at about 1330 and 720 cm^{-1}. This degeneracy is lifted by coordination and the two bands are split into separate components. The splitting of the 1330 cm^{-1} frequency into the asymmetric (ν_4) vibration at 1540 to 1610 cm^{-1}, and the symmetric (ν_1) vibration at 1300 cm^{-1} is indicative of covalent nitrato groups. The differences between these streching vibrations (ν_4-ν_1) of 240 to 310 cm^{-1} are expected for unidentate nitrato bonding[3].

The ionic nitrate absorption at 1330 cm^{-1} is observed in the spectrum and is due to hydrolysis of the compound. Unlike the tetranitratoborate compound the nitratoaluminates are hydroliticly unstable. Spectra (b) and (c) of Figure 1 are of the compound after exposure to air for increasing lengths of time. These show loss of C_{2v} symmetry, decreasing nitrato absorption at 1590 to 1610 cm^{-1} and stronger absorption at 1330 cm^{-1} of D_{3h} symmetry for ionic nitrate.

Ionic nitrate is also observed in the Raman spectra of the new compound. A large number of other bands are also present, however, the low signal to noise ratio in the spectra does not enable one to discern the true absorption bands, and assignments would be tentative at best. Further work must be done with the solid or solutions of the solid to make valid interpretations.

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(3)(a) K. W. Bagnell, D. Brown and J. G. H. duPreey, J. Chem. Soc., 5523 (1964).
(b) B. O. Field and C. J. Hardy, Quart. Rev. (London), 18, 385 (1964).
(c) G. Topping, Spectrochemica Acta., 21, 1743 to 1751 (1965).

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$[Me_4N]_3[Al(NO_3)_6]$ has a density of 1.40 gm/cc; obtained by pelletization in KBr at 115,000 lbs. per square inch. Its heat of formation is -530 ± 16 Kcal/mole; determined by the calorimetric measurement of the heat of hydrolysis:

$$[Me_4N]_3[Al(NO_3)_6] \xrightarrow{H_2O} 3\ Me_4N^+ + Al^{+++} + 6\ NO_3^- + \Delta$$

The compound is stable at room temperature but rapid decomposition occurs at 260 - 264°C without melting. It is insensitive to shock when struck sharply with a hammer.

As mentioned previously, the compound hydrolyzes rapidly in the atmosphere and in water. The solubility of $[Me_4N]_3[Al(NO_3)_6]$ in N_2O_4 is greater than 33 g/100 g N_2O_4 at approximately 25°C. The vapor pressure of the solution (575 mm) at this temperature was significantly depressed. Degradation of the hexanitrato complex occurred on prolonged contact with N_2O_4 (24 hours), the products were tetramethylammonium tetranitratoaluminate $[Me_4N][Al(NO_3)_4]$, oxygen, nitrogen, and carbon dioxide.

$[Me_4N][Al(NO_3)_4]$ analyzed as follows: calculated for $[Me_4N][Al(NO_3)_4]$: C, 13.76%; H, 3.47%; Al, 7.72%; Me_4N^+, 21.1%; N, (Devarda), 16.05%. Found: C, 15.6%; H, 4.4%; Al, 8.1%; Me_4N^+, 22.4%; N (Devarda), 15.12%. The X-ray powder diffraction pattern of the solid was obtained using Cu Kα radiation, however, the reflections were poor and not sufficiently discernable for accurate measurement. Although different, similarities can be observed when compared with the hexanitrato derivative.