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Annual Report

STUDIES OF
COMPLEX PERCHLORATES

ONR Nonr 3943(00) ✓

October 27, 1964

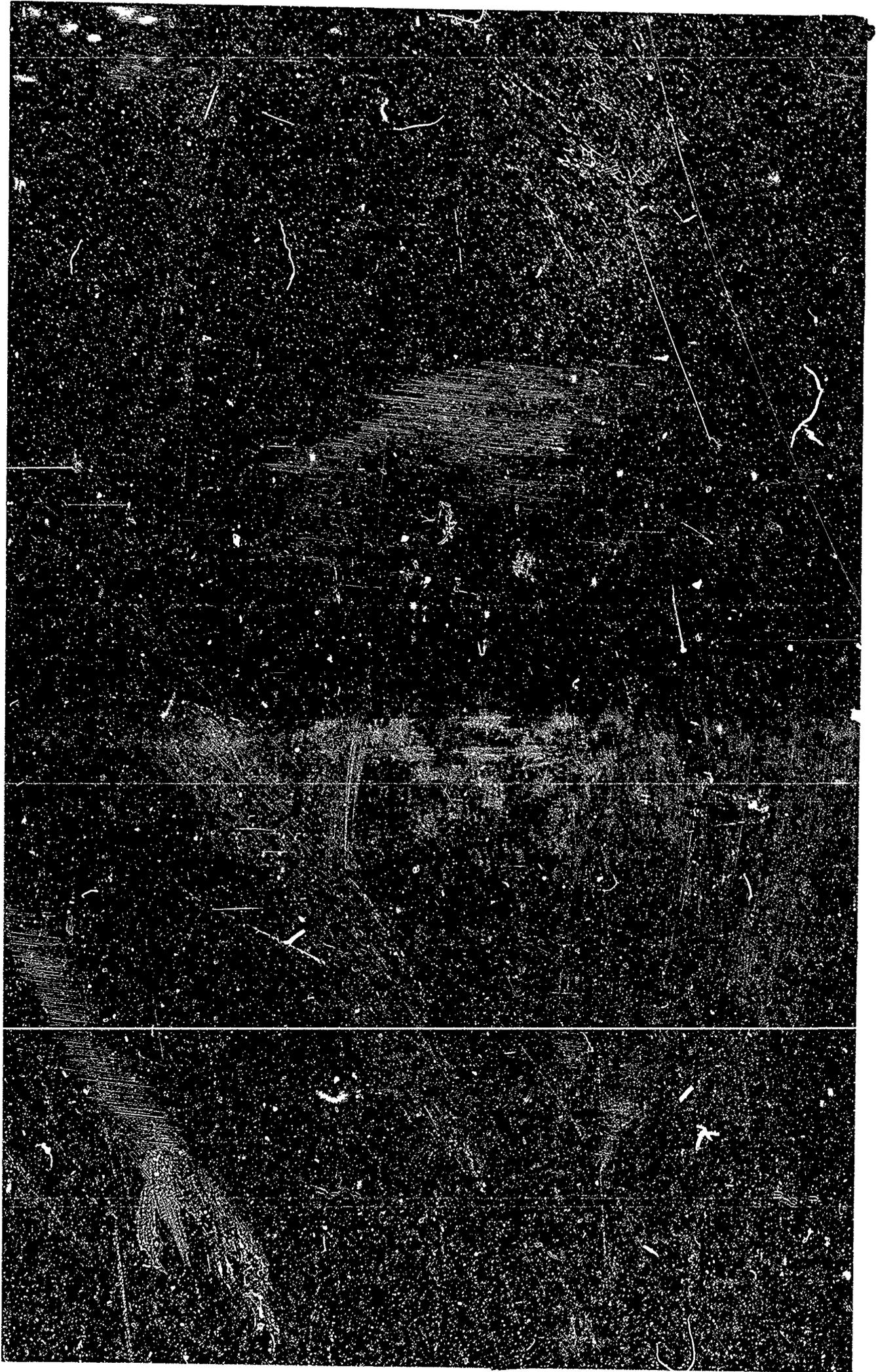
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STUDIES OF COMPLEX PERCHLORATES

ONR Nonr 3943(00)

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October 27, 1964

Callery Chemical Company
Callery, Pennsylvania

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ABSTRACT

Research in complex perchlorates is continuing. One complex perchlorate of beryllium $((\text{NO}_2)_2\text{Be}(\text{ClO}_4)_4)$ has been prepared and characterized, but efforts to prepare other beryllium derivatives were unsuccessful. A complex perchlorate having silicon as the central element could not be prepared. Preliminary efforts to synthesize $((\text{CH}_3)_4\text{N})_3\text{Al}(\text{NO}_3)_6$ have given encouraging results.

Infrared and Raman spectra of several complex perchlorates have been obtained. These spectra indicate covalent character on the part of the coordinated perchlorate group.

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STUDIES OF COMPLEX PERCHLORATES

INTRODUCTION

Research on complex perchlorates has continued under the sponsorship of the Office of Naval Research, Contract Nonr 3943(00). This report describes research carried out during the current annual contract period.

Recent effort has seen a shift in emphasis from a synthesis effort aimed at preparation of new compounds, to research directed at clarification of properties and structures of the complex perchlorates. A considerable effort has thus been devoted to attempts to obtain infrared and Raman spectra of available compounds. New synthesis work has involved additional complex perchlorates of zinc, and the hitherto uninvestigated central elements beryllium and silicon. In addition, a small effort was devoted to attempts to prepare definite complex nitrates of aluminum.

RESULTS AND DISCUSSION

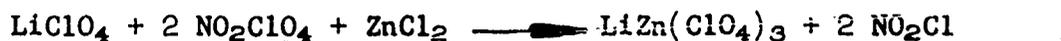
Complex Zinc Perchlorates

LiZn(ClO₄)₃ -- This compound was reported on a preliminary basis in the preceding annual report (1), but a completely satisfactory preparative method was not then available, and physical properties had not been adequately determined. In current research, two methods were investigated in some detail during the preparation of sufficient quantities of material for characterization. These methods proved to be satisfactory, but neither gave good purities with greater

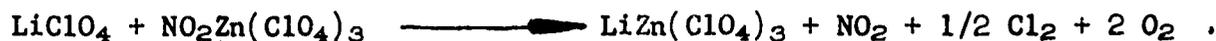
(1) Callery Chemical Company, Annual Report, Feb. 10, 1964, Studies of Complex Perchlorates, ONR Nonr 3943(00)

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than 2-3 gram batches. One method consists of premixing zinc chloride, lithium perchlorate and excess nitronium perchlorate in liquid sulfur dioxide at -10°C followed by heating under vacuum for several days at $120 - 125^{\circ}\text{C}$. The net reaction is



with excess nitronium perchlorate being decomposed to volatile materials. At intermediate stages, $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ was detected in the solids, and it is likely that this compound is first formed and then reacts slowly as shown by the equation



Products of very good purity were prepared by this method in 2 to 3 gram quantities.

The second preparative method involves the same reactants (LiClO_4 , NO_2ClO_4 and ZnCl_2) as above, but utilizes nitromethane as a reaction solvent. Sulfur dioxide and phosgene are unsuitable solvents, due apparently to the very low solubility of zinc chloride. Solubility relationships are more favorable in nitromethane, and elimination of chloride is complete in only a few hours. The product cannot be completely freed of nitromethane by evacuation at ambient temperatures. This can be effected at 125°C , however. In practice a slight excess of nitronium perchlorate is employed; the excess decomposes at the temperature (125°) used to remove nitromethane.

The nitromethane method has been used without incident in 1-2 gram runs. In one five gram run, the product prior to heating was a tacky solid which exploded and burned during an attempt to remove it from the flask. The method should thus

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be used with caution.

A typical preparation of $\text{LiZn}(\text{ClO}_4)_3$ is carried out as follows. Lithium perchlorate (1.58 g.), nitronium perchlorate (2.36 g.) and zinc chloride (0.74 g.) were stirred together in 20 ml of sulfur dioxide at -10° for two hours. Volatiles were evaporated, and residual solids were heated at 125° for 5 days under continuous evacuation. The weight (1.9 g) of recovered product represents a 95% yield of $\text{LiZn}(\text{ClO}_4)_3$. Observed (mat/g): Li, 2.68; Zn, 2.63; Cl, 8.0; N, 0.14. Theory: Li, 2.70; Zn, 2.70; Cl, 8.10.

The compound $\text{LiZn}(\text{ClO}_4)_3$ is usually pale yellow in color. Two density determinations, by displacement of Kel-F oil, yielded values of 2.78 and 2.85. No sensitivity to shock was observed. As usual with complex perchlorates, atmospheric moisture hydrolyzes $\text{LiZn}(\text{ClO}_4)_3$, and dissolution in water is accompanied by complete hydrolysis. Measurements of heats of hydrolysis yielded a calculated standard heat of formation of -148 ± 4 kcal/mol. The reaction



thus involves little or no net enthalpy change.

A density of 3.0 to 3.1 is calculated for zinc perchlorate if one assumes that $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ and $\text{LiZn}(\text{ClO}_4)_3$ are mixtures of zinc perchlorate and lithium or nitronium perchlorate. A density this high would indicate that the zinc ion, in zinc perchlorate, is effectively about the same size as the magnesium ion in magnesium perchlorate. Zinc is normally larger in radius or volume than magnesium. It appears therefore that in the complex zinc perchlorates the perchlorate groups

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are more efficiently packed together in the crystal lattices than is possible with zinc perchlorate. It would be of interest to obtain the density of zinc perchlorate in order to determine if this is indeed the case.

A distinctive x-ray diffraction pattern is exhibited by $\text{LiZn}(\text{ClO}_4)_3$. The patterns (d values, relative intensities) of $\text{LiZn}(\text{ClO}_4)_3$, $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$, and $\text{Zn}(\text{ClO}_4)_2$ are tabulated below.

<u>$\text{LiZn}(\text{ClO}_4)_3$</u>	<u>$\text{NO}_2\text{Zn}(\text{ClO}_4)_3$</u>	<u>$\text{Zn}(\text{ClO}_4)_2$</u>
7.00 S	6.40 VS	5.90 S
6.00 W	4.50 M	5.45 S
5.50 W	4.00 M	4.70 M
4.70 VW	3.65 M	4.20 VW
4.50 VW	3.40 M	3.80 S
4.10 M	3.19 S	3.50 S
3.80 W	2.85 MS	3.40 VW
3.60 VS	2.60 W	3.19 S
3.30 S	2.45 W	3.02 S
3.20 VW	2.25 M	2.85 M
3.02 M	2.00 M	2.80 M
2.80 M	1.76 W	2.70 VW
2.72 W	1.60 W	2.61 M
2.65 W	1.55 W	2.52 M
2.40 S		2.33 W
2.28 M		2.25 S

Solubility characteristics of $\text{LiZn}(\text{ClO}_4)_3$ are similar to those of $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$. Both are readily soluble in nitromethane, and insoluble in sulfur

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dioxide and phosgene.

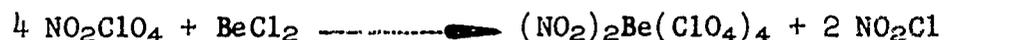
$\text{NH}_4\text{Zn}(\text{ClO}_4)_3$ -- This compound has not been prepared. Several obvious procedures were screened without success early in the contract period. Upon reviewing the work it was found that none of these procedures duplicated the method used to prepare $\text{LiZn}(\text{ClO}_4)_3$. The best result was obtained from the reaction system $\text{NH}_4\text{ClO}_4\text{-ZnCl}_2\text{-2 NO}_2\text{ClO}_4$ at 125° , but the product contained unreacted zinc chloride and ammonium perchlorate. With an excess of nitronium perchlorate it is expected that $\text{NH}_4\text{Zn}(\text{ClO}_4)_3$ and other derivatives can be prepared without difficulty.

Complex Beryllium Perchlorates

A fairly intensive study of beryllium as a central element has been carried out. Complexes sought were: $(\text{NO}_2)_2\text{Be}(\text{ClO}_4)_4$, $\text{Li}_2\text{Be}(\text{ClO}_4)_2$, $(\text{NH}_4)_2\text{Be}(\text{ClO}_4)_4$, and aluminum beryllium complexes such as $\text{Be}_3\text{Al}_2(\text{ClO}_4)_{12}$. In addition, certain products proved to be viscous liquids, and some effort was devoted to attempts to characterize these materials.

Beryllium chloride was employed as an intermediate. Commercially available beryllium chloride was not sufficiently pure. High purity beryllium chloride was obtained by sublimation at 300°C .

$(\text{NO}_2)_2\text{Be}(\text{ClO}_4)_4$ -- The compound proved to be quite soluble in sulfur dioxide. It can be prepared readily by reaction of an excess of nitronium perchlorate with beryllium chloride in sulfur dioxide via the reaction

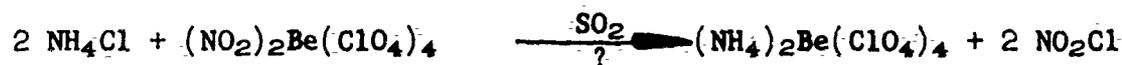
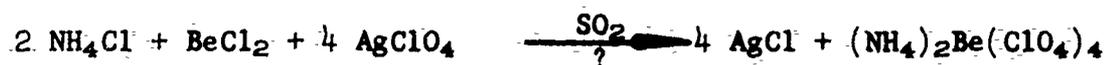
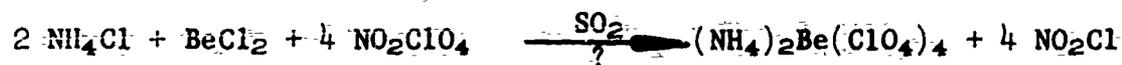
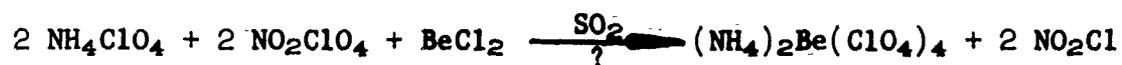


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Filtration yields an extract of $(\text{NO}_2)_2\text{Be}(\text{ClO}_4)_4$ which is recovered as a white crystalline solid by evaporation of volatiles. Theory: Be, 2.00; N, 4.01; Cl, 8.02 mats/g. Found: Be, 1.96, 2.01; N, 4.00, 4.05; Cl, 7.50, 7.53. The x-ray powder pattern (d values, relative intensities) is as follows: 6.50 (m), 4.90 (m), 4.60 (m), 3.65 (s), 3.50 (m), 3.25 (s), 2.90 (w), 2.70 (w), 2.55 (vw), 2.35 (vw), 2.25 (vw), 2.18 (w), 2.11 (vw). The density, measured by displacement of Kel-F oil, was 2.17-2.2 g/cc. The standard heat of formation was found to be -70 ± 6 kcal/mole by measurement of heats of hydrolysis.

The stability of $(\text{NO}_2)_2\text{Be}(\text{ClO}_4)_4$ is better than those of complex boron perchlorates and inferior to the stabilities of $\text{NO}_2\text{Zn}(\text{ClO}_4)_4$ and $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_3$. At room temperature it appears to be stable indefinitely. At 90° - 100°C decomposition occurs at a measurable rate; decomposition proceeds toward beryllium oxide, apparently through beryllium oxyperchlorates.

Attempted Synthesis of $(\text{NH}_4)_2\text{Be}(\text{ClO}_4)_4$ and $\text{Li}_2\text{Be}(\text{ClO}_4)_4$ -- Efforts to prepare these compounds were unsuccessful. Several reaction schemes were investigated, as illustrated by the equations below.



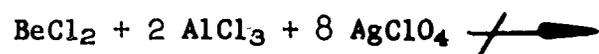
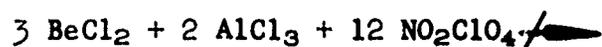
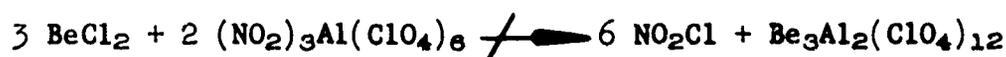
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In no instance, with either lithium or ammonium, was a product obtained with purity high enough that one could justifiably say that the desired compound had been prepared. In reactions involving nitronium perchlorate, $(\text{NO}_2)_2\text{Be}(\text{ClO}_4)_4$ was usually indicated by x-ray analysis. It was usual also to find x-ray evidence of uncomplexed lithium or ammonium perchlorate. Products were thus mixtures exhibiting no conclusive evidence of desired complex formation. In addition, loss of charged perchlorate was experienced. This indicates that some degradation to oxide occurred. This is to be expected if overall conditions are not ideal for formation of stable complex perchlorates. Less than ideal conditions permit formation of beryllium perchlorate, which is not expected to be stable.

A curious result was on occasion achieved. Liquid, sulfur dioxide soluble products were obtained under conditions favoring a complex of the type $\text{MBe}(\text{ClO}_4)_3$, where $\text{M} = \text{Li}$ or NH_4 . Analytical data gave a poor fit with the formula $(\text{MBe}(\text{ClO}_4)_3)_n$, however, and it was necessary to assume the presence of oxide. Efforts to further clarify these results were unsuccessful. It has been concluded that a high degree of polymeric character, through BeOBe and $\text{Be-OCLO}_2\text{O-Be}$ bonds, is responsible for the existence of these materials as liquids.

Attempted Synthesis of Aluminum-beryllium Complexes -- These were of interest in that proposed complexes would contain two small and highly charged elements. The probability for stability was, however, deemed only slightly greater than for either aluminum perchlorate or beryllium perchlorate. On the basis of the lack of success in preparing mixed complexes, the predicted marginal stability was borne out. Reactions typical of those attempted are illustrated by the following equations.

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These reactions generally yielded silver chloride or nitryl chloride as desired, but products invariably contained a substantial quantity of oxide by analysis. Degradation thus occurred, and product purities were low on the basis of expected products.

Attempted Preparation of $(\text{NO}_2)_2\text{Si}(\text{ClO}_4)_8$ -- Somewhat unexpectedly, it was found that silicon tetrachloride and nitronium perchlorate are unreactive either in a gas-solid system or in liquid sulfur dioxide or nitromethane. At higher temperatures (100°C) reaction occurred, but silicon dioxide was produced.

Complex Aluminum Nitrates

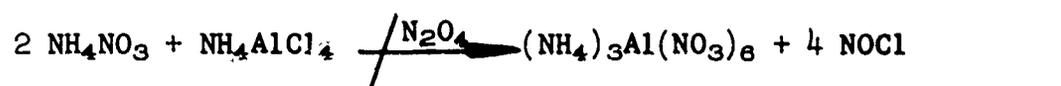
Complex nitrates analogous to complex perchlorates prepared in this program are well known, chiefly from the work of Addison (2) and co-workers. None of these contained a light metal such as aluminum as the central element. Earlier Callery research had shown that aluminum chloride reacted with liquid N_2O_4 to yield non-crystalline substances which by analyses could be construed to be mixtures of $\text{NOAl}(\text{NO}_3)_4$ and AlONO_3 . It was felt that definite complexes were possible if a second cation, such as NH_4^+ , were provided so that substances such as $\text{NH}_4\text{Al}(\text{NO}_3)_4$

(2) Addison and Hodge, J. Chem. Soc. 1138 (1954)
Addison, Hodge and Thompson, Ibid. 1143 (1954)

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or $(\text{NH}_4)_3\text{Al}(\text{NO}_3)_6$ could be formed. This possibility has been screened with ammonium and tetramethylammonium as the added cations.

The ammonium ion was generally unsuited for this purpose. The ion was apparently partially oxidized by liquid N_2O_4 in the reaction system



and a degraded product was obtained. In liquid phosgene no reaction occurred between NH_4AlCl_4 and either silver nitrate or N_2O_4 . Silver nitrate reacted with NH_4AlCl_4 in sulfur dioxide with elimination of most of the chloride as silver chloride, but the amorphous solid contained oxide by analysis.

The tetramethylammonium ion is more resistant to oxidation, and yields products having analyses close to values calculated for $((\text{CH}_3)_4\text{N})_3\text{Al}(\text{NO}_3)_6$. In liquid N_2O_4 at room temperature the reaction system $2((\text{CH}_3)_4\text{NNO}_3) - (\text{CH}_3)_4\text{NAlCl}_4 - \text{N}_2\text{O}_4$ yields a soluble product. Evaporation of volatiles gives a crystalline solid which evolves some nitrogen dioxide on standing. The analytical data ((mat/g) C, 19.1; H, 60.3; N, 14.9; Al, 1.35) compare favorably with theory (C, 19.3; H, 58.0; N, 14.5; Al, 1.60) with the exception of a low aluminum content. This suggests the presence, to the extent of 10% of the aluminum, of a compound such as $(\text{NO})_3\text{Al}(\text{NO}_3)_6$. Titrations of hydrolysates reveal little oxidizable material (NO^+), however, and it would thus appear that the contaminant should be a nitronium derivative ($(\text{NO}_2)_3\text{Al}(\text{NO}_3)_6$?). One does not expect a nitronium derivative to form in the presence of N_2O_4 , however.

There is no question that a complex tetramethylammonium aluminum nitrate has indeed been formed, as aluminum chloride in N_2O_4 forms the previously-mentioned,

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N_2O_4 insoluble, amorphous nitrate which appears by analysis to be a mixture of $NOAl(NO_3)_4$ and $AlONO_3$. The product from aluminum chloride contains less than four nitrate groups per aluminum in contrast to six observed in the presence of added tetramethylammonium ion. By analogy to the complex aluminum perchlorates, one expects higher stability (less tendency to degrade to aluminum oxynitrates through elimination of N_2O_5) for a tetracoordinate than a hexacoordinate derivative. This too appears to be borne out by the results. Further work is required, however, to prepare a higher purity material and to further characterize the complex.

SPECTRA OF COMPLEX PERCHLORATES

Information garnered in studies of various complex perchlorates leaves little room to doubt that the compounds should be considered to be somewhat unusual members of the large family of coordination compounds. They are unusual in two respects. Perhaps the most difficult-to-accept aspect of the compounds is that the perchlorate ion or group is classically thought to be a very weak coordinating ligand. The second unusual feature is the fact that, in this work, the very lightest of central elements have been used with success. The evidence of complex formation is, however, largely circumstantial in nature, and needs to be substantiated by measurements capable of more directly proving structure. The ultimate in evidence would of course be furnished by X-ray crystallographic studies. In the interim it is possible to obtain other evidence such as molecular weights, conductivities in non-aqueous solvents, and spectral characteristics which will serve to define compounds. During this report period a fairly intensive study of infrared spectra has been conducted, and some attention has been given to the obtaining of Raman spectra.

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Infrared Spectra

The relatively high reactivity of the complex perchlorates makes it mandatory that special techniques be employed to obtain spectra. Reaction with water, and the accompanying hydrolysis, proved to be the greatest problem. Nujol mulls, even with great care in handling, invariably showed some water contamination, though in some instances this was not severe. The most generally useful technique consisted of loading, in a dry box, a thin film of powder between two circular sodium chloride crystals which were then carefully taped to exclude atmospheric moisture. Infrared spectra so obtained usually exhibited little evidence of water.

Two reservations must, however, be kept in mind when considering the spectra. First, a small quantity of water may have a pronounced effect on the spectra. Water may in theory cause hydrolysis, as in the equation



in which case one would expect to see spectral evidence of perchloric acid. The other effect would be simple displacement of perchlorate by water, and in this case one would expect to see spectral evidence of perchlorate ion. This latter effect has been observed on deliberate exposure of samples to atmospheric moisture, and formation of perchlorate ion is believed to be the predominant result of limited hydrolysis. The second reservation involves the possibility of reaction between sodium chloride crystals and the compounds. Such reaction would also be expected to be productive of perchlorate. Hathaway and Underhill ⁽³⁾ state that this was a

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

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problem with several perchlorates studied by them. They eliminated this possibility by shielding compounds from salt windows by thin films of polyethylene. This technique is currently under investigation at Gallery.

The spectra of perchlorate ion and of covalently bonded ClO_4 in HClO_4 are recorded and have been interpreted. The article by Hathaway and Underhill (3) summarizes these spectra, and these authors have developed a treatment of ClO_4 spectra as it applies to the possibility of monodentate and bidentate coordination. Briefly, this treatment is as follows. The perchlorate ion is a regular tetrahedron belonging to the point group T_d . It exhibits a non-degenerate symmetrical stretch (ν_1) at 932 cm^{-1} , a doubly degenerate symmetric bending frequency (ν_2) at 460 cm^{-1} , a triply degenerate asymmetric stretch frequency (ν_3) at 1110 cm^{-1} , and a triply degenerate asymmetric bending frequency (ν_4) at 626 cm^{-1} . Of these, ν_3 and ν_4 are Raman and infrared active, while ν_1 and ν_2 are theoretically forbidden in the infrared. Usually, however, a very weak absorption occurs in the infrared at about 930 cm^{-1} (ν_1) due to distortion of the ion in the crystal field.

If the perchlorate group is monodentate, one oxygen atom now differs from the other three (O_3ClO^*), and the symmetry now becomes C_{3v} . Characteristic vibrational frequencies are expected to differ both in position and number, with the extent of the shift being a function of the strength of the coordinate bond. Hathaway and Underhill have developed a treatment of the types of vibrations expected for monodentate perchlorate, and have by analogy to perchloric acid and

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

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perchloryl fluoride made tentative assignments of characteristic frequencies. This treatment was employed in an interpretation of the spectra of acetonitrile complexes of transition metal perchlorates, and of lower hydrates of transition metal perchlorates. They conclude that in $\text{Zn}(\text{CH}_3\text{CN})_4(\text{ClO}_4)_2$ the perchlorate groups have deviated substantially toward monodentate covalency, and that this transition is essentially complete in $\text{Cu}(\text{H}_2\text{O})_2(\text{ClO}_4)_2$ and hydrates of other transition metal perchlorates. The hydrates contain two strong peaks between 1200 and 1000 cm^{-1} and a strong peak at 890 - 940 cm^{-1} . For $\text{Cu}(\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ the frequencies, with tentative assignments, are: 1158 (ν_4), doubly degenerate ClO^* asymmetric bending; 1030 (ν_1), non-degenerate ClO_3 symmetrical stretching; and 920 (ν_2), non-degenerate ClO^* symmetrical stretching. In contrast to a single frequency for ionic perchlorate in the potassium bromide region, $\text{Cu}(\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ exhibited three strong bands at 648 cm^{-1} (ν_3), 620 and 605 cm^{-1} (ν_5) and a weaker band at 480 cm^{-1} (ν_8).

Hathaway and Underhill similarly examined the possibility of a bidentate ($^*\text{OClO}_2\text{O}^*$) perchlorate group. This group has the symmetry C_{2v} . Bidentate character was exhibited by anhydrous copper perchlorate. By analogy with bidentate sulfate and with sulfuryl fluoride observed frequencies were tentatively assigned as follows.

1270 - 1245 sb:	non-degenerate ClO_2^* antisymmetric stretching	(ν_8)
1130 s:	non-degenerate ClO_2 antisymmetric stretching	(ν_6)
1030 w:	non-degenerate ClO_2 symmetrical stretching	(ν_1)
948 s, 920 s:	non-degenerate ClO_2^* symmetrical stretching	(ν_2)
665 m, 647 m:	non-degenerate ClO_2 , symmetrical bending	(ν_3)
624 m, 600 s:	non-degenerate rocking	(ν_7)
497 m:	non-degenerate rocking	(ν_9)
466 w:	non-degenerate ClO_2^* symmetrical bending	(ν_4)

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The infrared spectra of various of the complex perchlorates prepared at Callery have been obtained only for the sodium chloride region. These spectra have been compared with those reported by Hathaway and Underhill to determine if possible something of the nature of bonding. For our purpose the important aspects of the Hathaway treatment are the observation of four bands in the 1300-900 cm^{-1} region for presumably bidentate perchlorate, and of three bands for monodentate perchlorate in the same region.

Spectra obtained for various complex perchlorates are tabulated below. The spectra of $\text{Cu}(\text{ClO}_4)_2$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$ ⁽³⁾ are included for purposes of comparison.

<u>$\text{NO}_2\text{Zn}(\text{ClO}_4)_3$</u>	<u>$\text{LiZn}(\text{ClO}_4)_3$</u>	<u>$(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$</u>	<u>$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$</u>	<u>$\text{Li}_3\text{Al}(\text{ClO}_4)_6$</u>
1210 s	1180 m	1180 sb	1180 sb	1200 s
1135 s	1110 s	1130-1080 m	1110 s	1165 sh
1030 s	1040 s	1040 s	1030 s	1060 s
958 m	960 m	925 ms	920 ms	1045 sh
945 m				950 s
670 m	670 m	685-670 (?) m		680 m

<u>$\text{NO}_2\text{Al}(\text{ClO}_4)_4$</u>	<u>$\text{Cu}(\text{ClO}_4)_2 \cdot 2 \text{H}_2\text{O}$</u>	<u>$\text{Cu}(\text{ClO}_4)_2$</u>
1190 sb	1158 vs	1270-1245 sb
1040 s	1030 vs	1130 s
925 s	920 vs	1030 w
	660 w	948 s
		920 s
		665 m

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Inspection of the spectra reveals that the ordinarily very weak absorption observed in the region of 930 cm^{-1} is much stronger with the complex perchlorates, and that the single strong band at about 1100 cm^{-1} has been split into two to three usually quite strong bands. This behavior is quite similar to that observed with the copper perchlorates. There thus can be no doubt that the perchlorate groups in the complex perchlorates are in bond environments which have altered the symmetry exhibited by the ClO_4^- ion.

Two compounds, $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ and $\text{LiZn}(\text{ClO}_4)_3$, clearly exhibit spectra typical of bidentate perchlorate as proposed by Hathaway. This is particularly true of $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$, which shows three sharp and strong bands at 1210, 1135 and 1030 cm^{-1} in addition to two weaker bands at 958 and 945 cm^{-1} .

The spectra of $\text{NO}_2\text{Al}(\text{ClO}_4)_4$ and $\text{Li}_3\text{Al}(\text{ClO}_4)_6$ by analogy indicate monodentate perchlorate. The two remaining complexes, $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ and $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$, yielded spectra closer in general features to the spectrum expected of bidentate perchlorate groups; this is particularly true of $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$, for which three strong bands were found in the 1000 to 1200 cm^{-1} region.

It is of course not unexpected that the evidence indicates bidentate character for the zinc perchlorates. Sharing of perchlorate groups in a manner giving in effect either a tetra or hexacoordinate structure is to be expected. One would predict as well a certain amount of bidentate character in $\text{NO}_2\text{Al}(\text{ClO}_4)_4$ which does not seem to be indicated by the spectra. In the hexaperchlorates of aluminum, it does not seem possible that bidentate character should be indicated, as in $(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$ and $(\text{NH}_4)_3\text{Al}(\text{ClO}_4)_6$, and it suggested that absorption at about

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1100 cm^{-1} for these two compounds may be due to perchlorate ion. If this is the case, perchlorate ion may have been formed by partial hydrolysis or by reaction with the sodium chloride windows. It is possible that one or more of the six perchlorate groups is essentially ionic; this does not seem likely, as the spectrum of $\text{Li}_3\text{Al}(\text{ClO}_4)_6$ indicates the absence of purely ionic perchlorate.

The nature of the infrared spectra is more clearly shown in Figures I, II and III. Of particular interest is the effect of absorption of water by $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ as shown in Figure III; as water is absorbed there is a gradual elimination of peaks at 1210, 1030 and 950 cm^{-1} accompanied by an apparent shift of the 1135 cm^{-1} absorbance to a strong peak at 1115 cm^{-1} typical of ionic perchlorate.

Also of interest is the infrared spectrum of magnesium perchlorate presented in Figure II. It was felt that magnesium perchlorate, with its small, doubly charged cation, should exhibit spectral evidence of covalent character. "Anhydrous" magnesium perchlorate failed to exhibit little more than a considerable broadening of the 1100 cm^{-1} peak, with very weak indications of additional peaks. The spectrum of Figure II was obtained by vacuum drying, at 200°C, a film of powder already in place on sodium chloride windows followed by scanning with minimum exposure through handling. The spectrum still exhibits a strong peak at 1100 cm^{-1} , and contains in addition well resolved peaks at 1210 and 980 cm^{-1} .

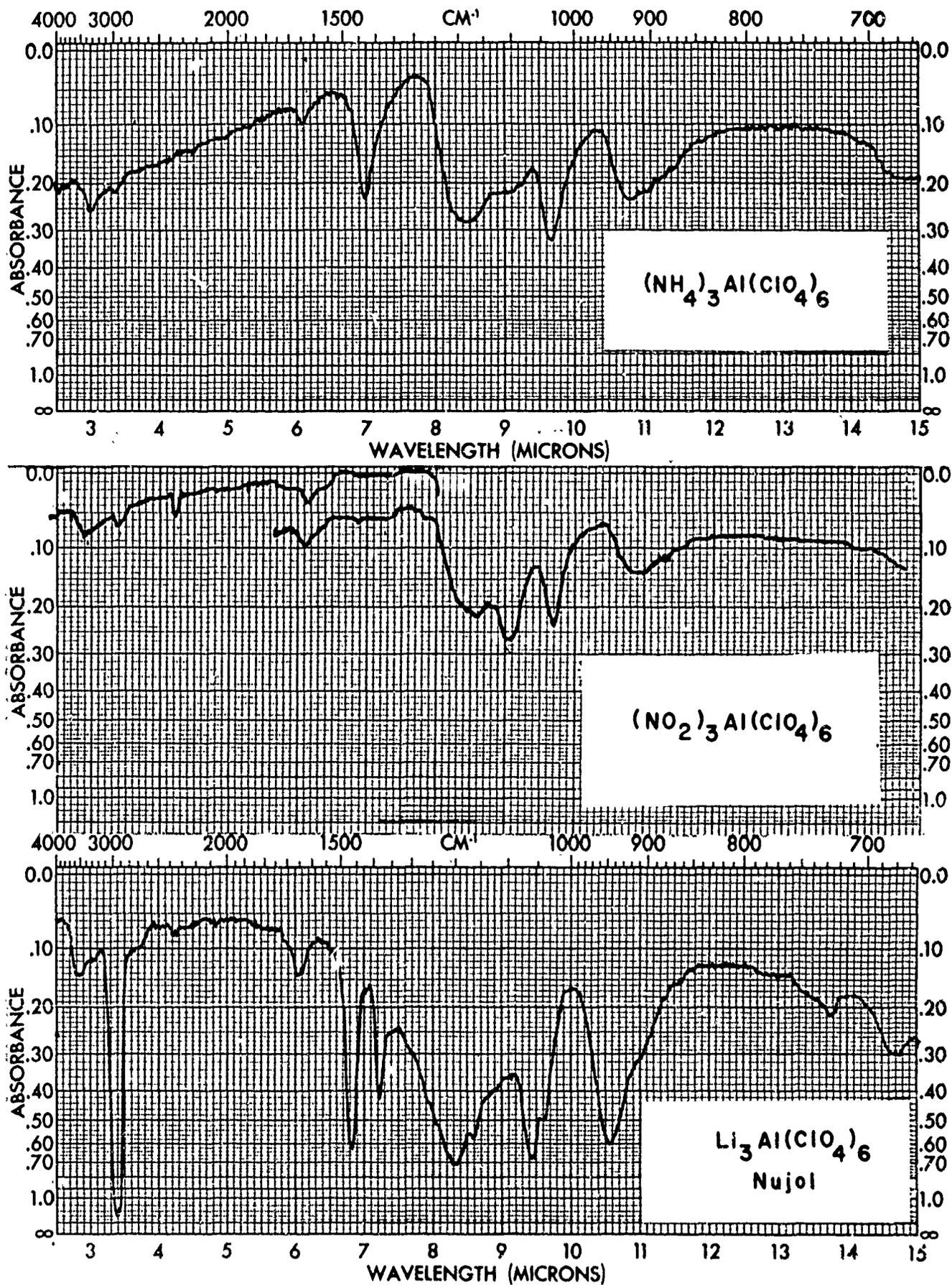


FIGURE I

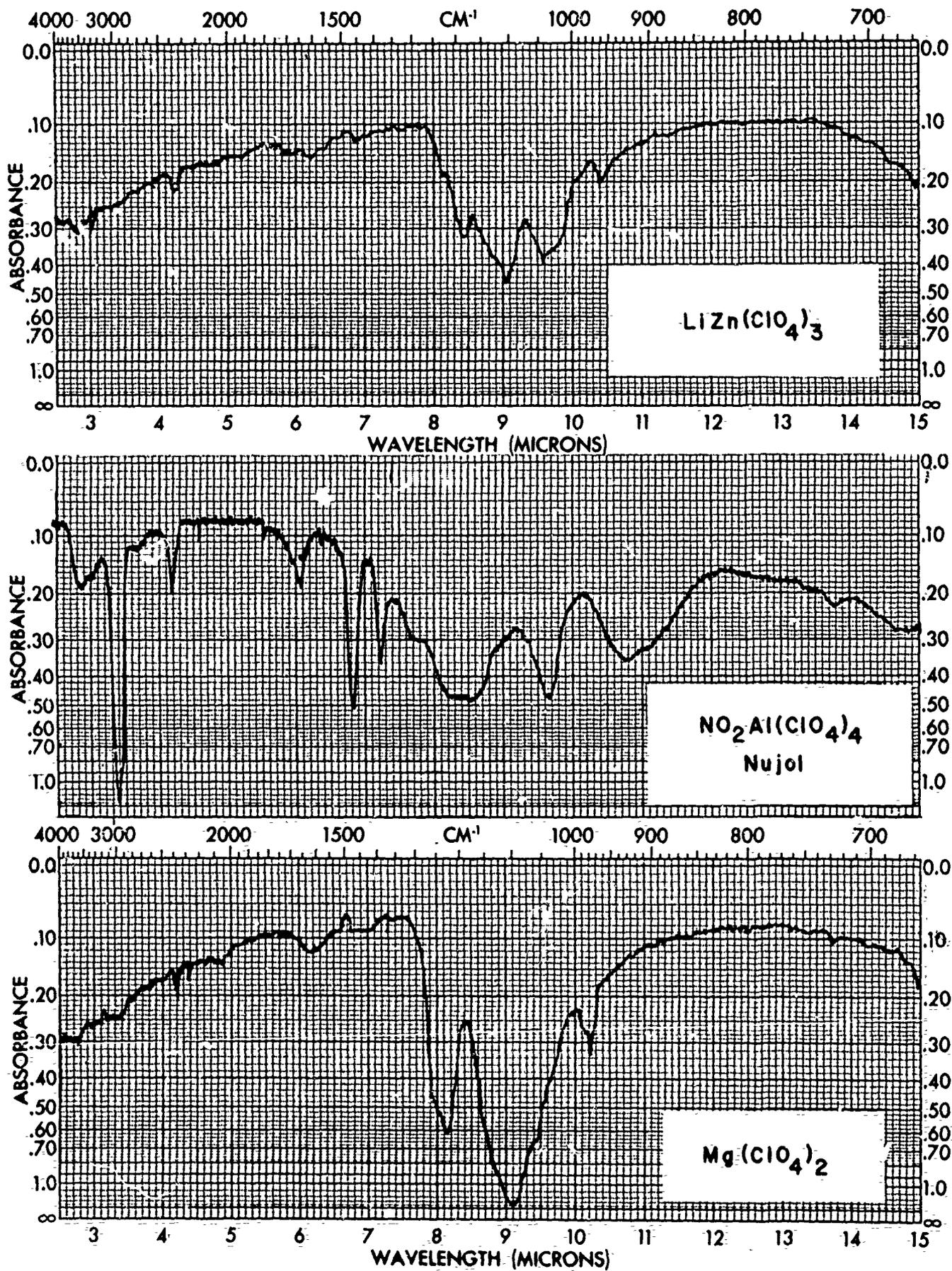


FIGURE II

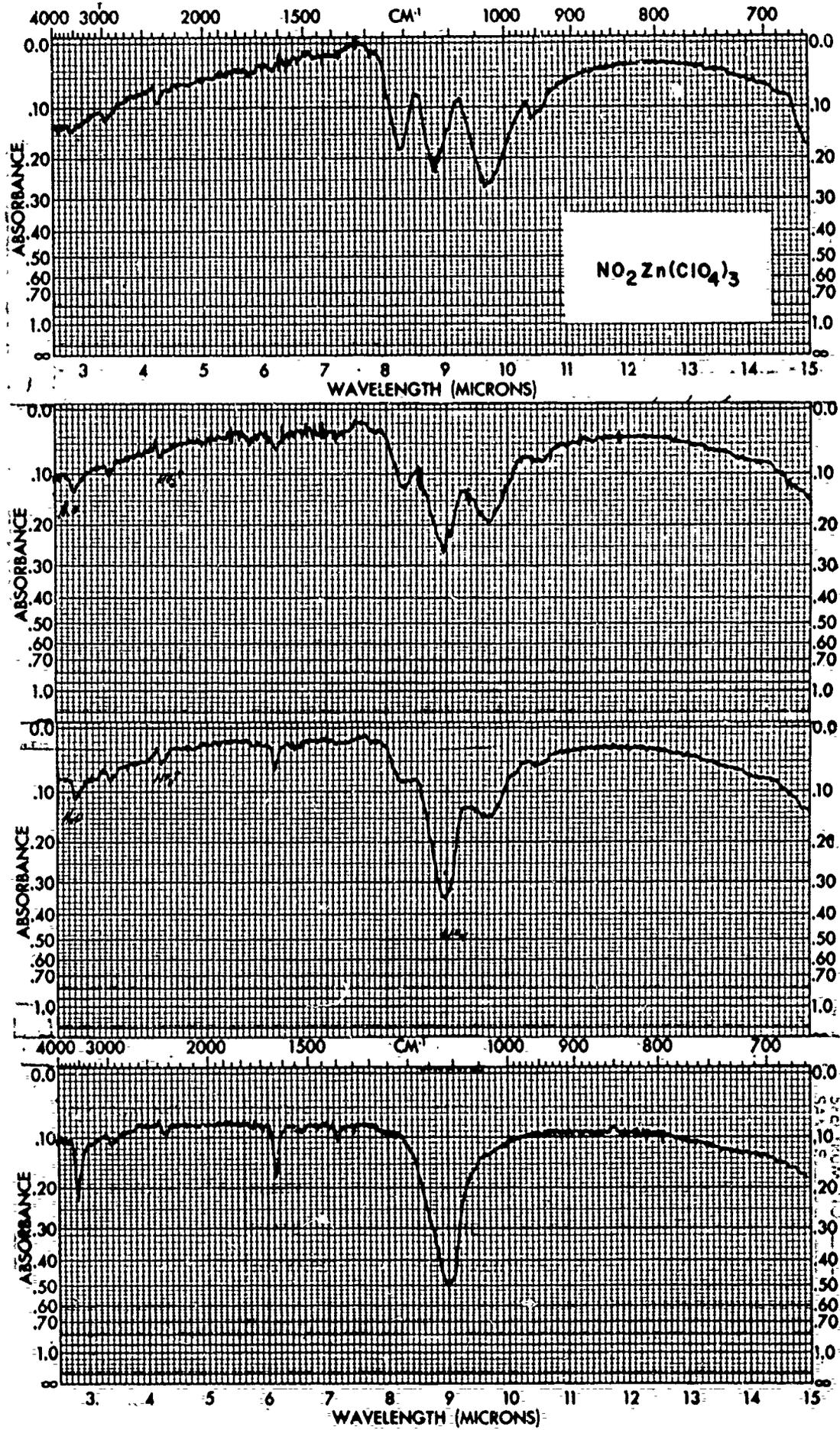


FIGURE III

The Effect On $\text{NO}_2\text{Zn}(\text{ClO}_4)_3$ Of Increasing Exposure To The Atmosphere

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Raman Spectra

It has generally been difficult to obtain well resolved Raman spectra of the complex perchlorates. This is a consequence of the fact that solids rather than liquids or solutions have been employed, and it is difficult with solids to obtain the proper combination of particle size, sample thickness and geometry, and placement in the optic system of the spectrometer. In early work thin layers (1-2 mm) of solids were placed on the inside of the optically flat end of a Raman sample tube. Later it was found that better response and resolution could be obtained in a tube containing a cone () which permitted the solids to be present in layers of varying thickness. Raman spectra obtained for several complex perchlorates as well as for nitronium perchlorate and nitrosonium perchlorate are shown below. Relative intensities are indicated by the numbers in parentheses.

RAMAN SPECTRA OF PERCHLORATES

<u>NOClO₂</u>	<u>NO₂ClO₄</u>	<u>NO₂Al(ClO₄)₄</u>	<u>(NO₂)₃Al(ClO₄)₆</u>	<u>NO₂Zn(ClO₄)₃</u>	<u>NO₂Be(ClO₄)₄</u>
460 (23)	448 (15)	460 (16)	485 (19)	450 (14)	
	471 (20)			480 (14)	
	571 (5)		627 (12)		
	625 (13)	635 (14)	670 (4)	615 (19)	
	640 (11)	680 (9)	940 sh	670 (7)	
930 (44)	936 (70)	970 (25)	970 (47)	960 (55)	945 (29)
	1080 (8)		1110 (8)	1130 (10)	
	1095 (8)		1180 (17)	1200 (10)	
	1139 (11)		1215 (14)	1400 (20)	1400 (18)
2300 (100)	1396 (69)	1400 (22)	1398 (36)		

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The Raman lines at $1396-1400\text{ cm}^{-1}$ are typical of the nitronium ion, while the 2300 cm^{-1} line for nitrosonium perchlorate is due to the nitrosonium ion. The remaining lines are all attributed to ionic or covalent perchlorate.

A surprising feature of the spectra is the high degree of resolution and fine structure exhibited by nitronium perchlorate. This compound has classically been assumed to contain strictly ionic perchlorate, in spite of the fact that crystal data show distortion of both the perchlorate ion and the nitronium ion. The general nature of the Raman spectrum of nitronium perchlorate gives a surprisingly good fit with the type of spectrum predicted by Hathaway for bidentate perchlorate. This quite naturally provokes questions about the validity of the assumption that the spectra are truly indicative of covalent character on the part of the perchlorate group. There is no reason to question the conclusion that the Raman spectrum of nitronium perchlorate is indicative of distortion of perchlorate ion, and probably in such a manner that it appears to be bidentate. On the other hand, observance of such behavior with nitronium perchlorate indicates that actual bonding can be considerably removed from true covalency, and still give spectral evidence formally interpretable as indicative of covalent bonds. In general, this is the interpretation preferred by the authors as it is applied to complex perchlorates. The perchlorate groups, in the complexes, are believed to form what may be considered to be weak covalent bonds, which means in turn that a strong metal to oxygen bond does not exist. Such bonding is still capable of producing interactions which distort the ClO_4 tetrahedron sufficiently that marked differences in spectra are observed. Apparent monodentate or bidentate character is thus as much a manifestation of the environment in which the perchlorate group finds itself as it is of the specific type of bonding.

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The Raman spectra of the complex perchlorates tabulated above show less fine structure than does the spectrum of nitronium perchlorate. The nitronium ion is shown to be present in all cases by the line at about 1400 cm^{-1} , and the line at $940\text{-}970\text{ cm}^{-1}$ was strongly observed in all cases. In the $1000\text{-}1200\text{ cm}^{-1}$ region, all the complexes absorbed strongly in the infrared but weakly in Raman. Weak to medium strength Raman lines were found at $450\text{-}480\text{ cm}^{-1}$ and $615\text{-}680\text{ cm}^{-1}$. Interpretation of the Raman spectra in terms of monodentate or bidentate character leads to apparent inconsistencies and some conflict with infrared evidence. These interpretations are as follows.

$\text{NO}_2\text{Al}(\text{ClO}_4)_4$: Raman lines at 460 , 635 and 680 cm^{-1} indicate monodentate character, as does the infrared.

$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$: Three Raman lines at 1110 , 1180 and 1215 cm^{-1} may be compared to three infrared peaks at 1030 , 1110 , and 1180 cm^{-1} . The positions are shifted $35\text{-}80\text{ cm}^{-1}$ on going from infrared to Raman. A similar shift in the same direction is also observed for 920 (IR) and 970 (R). These Raman lines are consistent with bidentate perchlorate.

The Raman lines at 485 , 627 and 670 cm^{-1} are on the other hand indicative of monodentate character, so the Raman evidence is apparently self inconsistent and only partially in agreement with infrared.

$\text{NO}_2\text{Zn}(\text{ClO}_4)_3$: The Raman spectrum indicates bidentate character, although one line is missing in the $600\text{-}700\text{ cm}^{-1}$ region, and another is lacking in the $1000\text{-}1200\text{ cm}^{-1}$ region. The two lines at 450 and 480 cm^{-1} may be sufficient evidence of bidentate perchlorate.

$(\text{NO}_2)_2\text{Be}(\text{ClO}_4)_4$: The Raman spectrum is obviously weak, as only one line

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for perchlorate was observed. This is illustrative of a reason for reservations concerning interpretation of Raman spectra at this time. With solids it is difficult to obtain good spectra with high signal strength, and one is not certain that resultant spectra are adequate for interpretative purposes.

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