dominant, and the magnetic behavior shown in Figure 1 would be observed.

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

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Chlorine Perchlorate

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

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

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

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

Experimental Section

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

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

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

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

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

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

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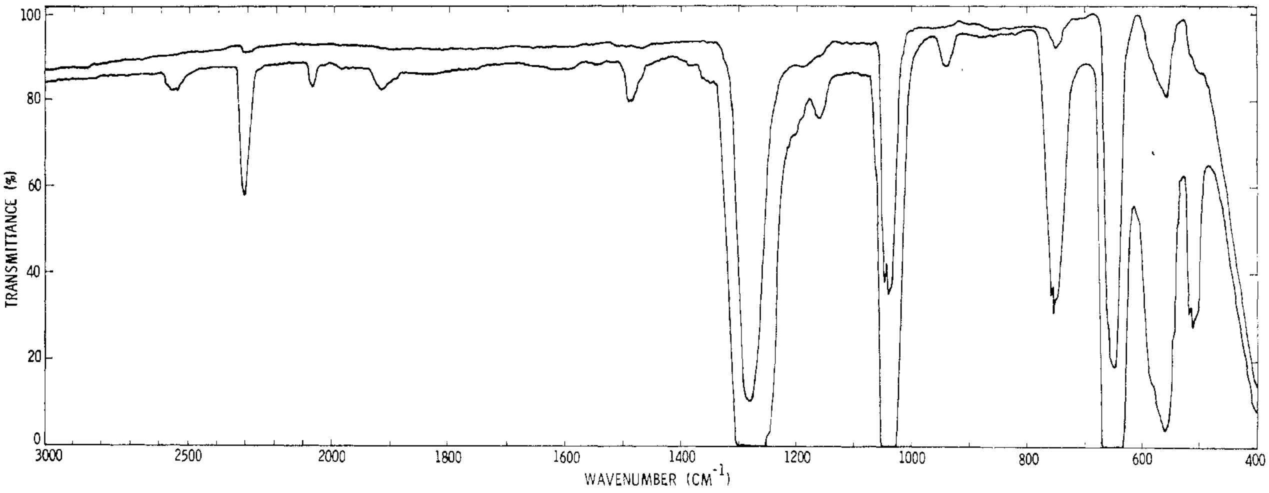

Figure 1.—Infrared spectrum of $ClOClO_3$ at 180 and 8 mm; 5-cm path.

(mm)]: −46.8, 8; −31.3, 21; −24.2, 32; 0.0, 119; 5.0, 150; 11.2, 202; 18.9, 283; 20.9, 305. The vapor pressure–temperature relationship is described by the equation log $P_{\text{mm}} = 7.8156 - 1568.0/T$°K. The normal boiling point calculated from the equation is 44.5°, with a heat of vaporization of 7.17 kcal/mol and a Trouton constant of 22.6.

Melting Point.—Samples of $ClOClO_3$ frozen as a ring in the upper part of a Teflon tube were observed to melt at −117 ± 2°.

Density.—The densities measured in a Pyrex pycnometer at −78.8, 0.0, and 21.2° were 1.98, 1.82, and 1.75 g/ml, respectively. Over this temperature range the density ρ is given by the equation: $\rho = 1.806 - 2.30 \times 10^{-3}t$°C.

Infrared Spectrum.—The infrared spectrum was recorded in stainless steel or Kel-F cells fitted with AgCl windows over the range 4000–400 cm^{-1} at a variety of pressures. Spectra are shown in Figure 1 at two pressures. The principal bands observed are 1282 (vs), 1041 (s), 752 (w), 661 (sh), 652 (s), 585 (sh); 574 (sh), 561 (m), and 511 cm^{-1} (w).

Reactions of $ClOClO_3$. Reaction with Hydrogen Chloride.—A Pyrex ampoule was loaded with $ClOClO_3$ (36.2 cm^3, 1.62 mmol) and HCl (42.6 cm^3, 1.90 mmol) at −196°. After maintaining the ampoule at −78° for 1 hr, separation of the products was initiated by first pumping the −78° volatiles through U traps cooled to −142 and −196° and later changing the ampoule to −45° while continuing to pump through the cold traps. The −196° trap contained unreacted HCl (6.0 cm^3, 0.27 mmol) while the −142° trap contained only Cl_2 (36.4 cm^3, 1.62 mmol). After warming the ampoule to room temperature, the weight of material retained at −45° was determined and this material was transferred to the vacuum line. It was identified as $HClO_4$ (0.155 g, 1.54 mmol) by its vapor pressure[8] and infrared spectrum.[9]

Reaction with AgCl.—A sample of $ClOClO_3$ (7.9 cm^3, 0.35 mmol) was loaded in a Kel-F infrared cell fitted with AgCl windows. On standing at ambient temperature for several hours, the $ClOClO_3$ was consumed leaving a thin deposit on the windows which was identified as ClO_4^- by its infrared spectrum.[5] No other infrared absorbing material was detected. After 1 day, the contents of the cell were analyzed by gas chromatography and found to be pure Cl_2 (7.5 cm^3, 0.33 mmol).

Decomposition in Pyrex.—Chlorine perchlorate (42.6 cm^3, 1.90 mmol) was condensed into a 150-cm^3 Pyrex bulb (equipped with a Fischer–Porter Teflon needle valve and a metal-to-glass seal to eliminate greased closures or connections) at −196°. The bulb was allowed to warm to room temperature in a closed, dark, steel can and to stand for several days. At this time, the bulb was observed to contain a small puddle of a red, somewhat viscous liquid. The contents were rapidly vacuum fractionated through traps cooled to −78, −112, and −196°. An unmeasured but appreciable amount of gas not condensable at −196° was observed. The other volatile products were Cl_2 (19.0 cm^3, 0.85 mmol), ClO_2 (9.9 cm^3, 0.44 mmol), and $ClOClO_3$ (~1 cm^3) as identified by their vapor pressure and/or infrared spectra. The red liquid was not readily pumped out of the bulb and exhibited a low (1–2 mm) vapor pressure at ambient temperature. On standing at ambient temperature, the liquid slowly generated Cl_2, ClO_2, and noncondensable gases. From these observations the liquid was identified as Cl_2O_6.[10] Based on one Cl_2O_6 from two $ClOClO_3$ molecules, the Cl_2O_6 yield was approximately 80%.

A similar experiment in which the Pyrex bulb was of much smaller volume (~20 cm^3) was examined after 2 days. The charged $ClOClO_3$ (53.5 cm^3, 2.39 mmol) was completely decomposed giving much O_2, Cl_2 (41.0 cm^3, 1.83 mmol), and ClO_2 (18.6 cm^3, 0.83 mmol). Only a small droplet of the red, liquid Cl_2O_6 was observed which, considering the chlorine evolved as Cl_2 and ClO_2, could not have amounted to >12% yield.

Photolysis.—Chlorine perchlorate (35.3 cm^3, 1.58 mmol) was condensed into a 200-cm^3 quartz bulb at −196°. The bulb was warmed to room temperature and irradiated with uv light overnight (Hanovia 100-W utility lamp, Catalog No. 30620). After recooling to −196°, the noncondensable gases were measured (32.8 cm^3, 1.46 mmol) and identified as O_2 by mass spectroscopy. Fractional condensation of the remaining material at −78 and −196° gave Cl_2 (24.8 cm^3, 1.11 mmol) and Cl_2O_7 (10.2 cm^3, 0.46 mmol) as the only detectable products. Chlorine heptoxide was identified by its vapor pressure and infrared spectrum.[11] Based on one Cl_2O_7 from two $ClOClO_3$ molecules, the yield was 58%.

Results and Discussion

Four reasonably stable oxides of chlorine are known and have been well characterized:[12] Cl_2O, ClO_2, Cl_2O_6, and Cl_2O_7. More recently, a fifth compound of very limited stability has been reported[13] with the empirical formula $ClO_{1.5}$ and the postulated composition $OClClO_2$. The new chlorine oxide, $ClOClO_3$, reported here was first obtained some time ago by the reaction of ClF and perchlorate salts at −78 or −45°

$$MClO_4 + ClF \longrightarrow MF + ClOClO_3 \quad (M = Cs, NO_2)$$

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However, the yields from these reactions were low (~5%) and somewhat irreproducible allowing only a tentative identification based on infrared data. The discovery of the present high-yield synthesis confirmed the nature this low-yield product and facilitated its characterization.

Caution! While no incidents were encountered during this work, chlorine perchlorate should be treated with all safety precautions appropriate to the use of any chlorine oxide. It is shock sensitive.[14]

Chlorine perchlorate has been identified by its vapor density, elemental analysis, and infrared spectrum. A stable mass-cracking pattern was not obtained but prominent *m/e* peaks for ClO_3^+, ClO_2^+, and ClO^+ were found. The absence of a parent ion peak is not surprising in view of its near absence in the reported[15] mass spectrum of Cl_2O_7, for example. The basic physical and chemical properties have been determined and all data are consistent with the formulation $ClOClO_3$.

Alternate structural formulations for the compound were ruled out on the basis of the infrared spectrum, Figure 1, and the chemical reactions discussed later. The strong bands at 1282 and 1041 cm^{-1} are readily assignable to the ClO_3 antisymmetric and symmetric stretching vibrations. The position, shape, and relative intensity of these two bands are remarkably similar to those of $HOClO_3$[9] (1263 and 1050 cm^{-1}), $O_3ClOClO_3$[11] (1309 and 1025 cm^{-1}), and $FOClO_3$[16] (1298 and 1049 cm^{-1}) and thus are indicative of a covalent perchlorate group. Furthermore, the exact position of the strongest observed ClO_3 antisymmetric stretching vibration correlates well with the electronegativity of the attached group. For the series of $XClO_3$ compounds, where X is F, O_3ClO, FO, HO, this band is located, respectively, at 1315, 1309, 1298, and 1263 cm^{-1}. The position of this band for chlorine perchlorate (1282 cm^{-1}) is compatible with this correlation, further supporting the assigned structural formula. Other noteworthy bands for $ClOClO_3$ are at 752 and 652 cm^{-1}. These bands are assignable to stretching modes of the Cl–O–Cl link. Comparable terminal Cl–O absorptions are found at 720 and 703 cm^{-1} for SF_5OCl[17] and $ClOSO_2F$[18] while $FOClO_3$ has a strong band at 666 cm^{-1} which has been ascribed[15] to its singly bonded chlorine–oxygen stretching vibration. A detailed analysis of the vibrational spectrum of $ClOClO_3$ is in progress.[19]

Reaction of $ClOClO_3$ and HCl occurred rapidly and nearly quantitatively

$$HCl + ClOClO_3 \xrightarrow{-78^\circ} Cl_2 + HClO_4$$

However, with AgCl large variations in the reaction rate were noted although the same final result was reached

$$AgCl + ClOClO_3 \longrightarrow Cl_2 + AgClO_4$$

Several factors including the surface state of the AgCl and trace impurities in the $ClOClO_3$ may account for this. In general this reaction was slower than the corresponding AgCl–$ClSO_3F$ reaction.[3] The products from both of these chloride reactions conclusively support the postulated perchlorate structure derived from infrared data.

The thermal stability of $ClOClO_3$ at ambient temperature is limited with either glass or stainless steel containers. A preparation conducted at ambient temperature in stainless steel gave no $ClOClO_3$ but a nearly quantitative yield of its elemental decomposition products. Pure $ClOClO_3$ also decomposed readily in Pyrex in the absence of light. Yields of the products of this decomposition differed greatly with the container volume and may have been influenced by other unknown variables, but a high conversion to Cl_2O_6 (80%) was possible. The only other chlorine oxide found was ClO_2, the other products being Cl_2 and O_2. The preparation of Cl_2O_6 by the thermal decomposition of $ClOClO_3$ may be an attractive alternate to the presently used photolysis of ClO_2 and O_3.[12]

Irradiation of $ClOClO_3$ in quartz at ambient temperature produced Cl_2O_7 in a reaction approximating the stoichiometry

$$7ClOClO_3 \longrightarrow 5Cl_2 + 7O_2 + 2Cl_2O_7$$

Formation of Cl_2O_7 directly by recombination of ClO_4 and ClO_3 radicals generated from $ClOClO_3$ is possible. However, Cl_2O_7 can also result[20] from irradiation of Cl_2O_6, which as noted above can be formed from $ClOClO_3$.

The overall stability of $ClOClO_3$ approaches that of the four well known chlorine oxides and is quite unlike that of the analogous compound $FOClO_3$ which tends to explode on freezing or during other simple operations.[21] This behavior trend is comparable to that of $FONO_2$[22] *vs.* $ClONO_2$.[23] However, it is the opposite of the general stability found[17,24–26] for highly fluorinated FO- and ClO-substituted compounds, CF_3OF *vs.* CF_3OCl or SF_5OF *vs.* SF_5OCl, where the ClO derivatives are less stable.

Using the known heats of formation (kcal/mol) of $FOClO_3$[27] (+37.6) and those of the related pairs of compounds, OF_2[28] (+5.5)–Cl_2O[29] (+21.0) and $FONO_2$[27] (+2.5)–$ClONO_2$[30] (+7.0), the heat of formation of

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[14] In a crude sensitivity test, approximately 0.15 ml of liquid $ClOClO_3$ was sealed in a small Pyrex tube. A 2-lb hammer dropped on the tube from approximately a 4-in. height resulted in a sharp explosion.

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$ClOClO_3$ was estimated as approximately +43. This value is reasonable, in view of the heats of formation of ClO^{29} (+24) and $ClO_3{}^{28}$ (+37), since the formation of the $ClO{-}ClO_3$ bond should be somewhat exothermic.

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Antiferromagnetism in Transition Metal Complexes. III. The Ground and Low-Lying Excited States of Cupric Acetate[1]

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The effects of the crystalline field and of electron repulsion on the energies of the low-lying electronic states of cupric acetate are discussed. These states, in order, are $^1A_{1g}$, $^3A_{2u}$, and $^1A_{1g}$, the lowest $^1A_{1g}$ and $^3A_{2u}$ states most probably arising from the occupation of $d_{x^2-y^2}$ orbitals and the other $^1A_{1g}$ arising from d_{z^2} orbitals. This leads to excellent agreement with the observed temperature dependence of the susceptibility.

It has been known for over 50 years that the molar susceptibility of cupric acetate monohydrate is appreciably less than that commonly found for copper(II) salts.[2a] The susceptibility of single crystals reaches a maximum at *ca.* 255°K and probably obeys the Curie–Weiss law at temperatures well above this,[2b] although the thermal decomposition of the compound has prevented this being observed experimentally, data being available up to 390°K. The explanation of this antiferromagnetic behavior undoubtedly lies in the existence of the compound as dimeric molecules both in the crystal state and in solution, the copper–copper separation[3] being *ca.* 2.64 Å (*cf.* metallic copper in which the separation is 2.56 Å), leading to a coupling between the unpaired electrons formally associated with each copper atom.

Dimeric copper(II) carboxylates, for which cupric acetate is the prototype, have attracted considerable attention, both experimentally and theoretically.[4] Experimentally, a wide range of stable species may readily be prepared which are susceptible to investigation by a range of techniques. Theoretically, the two copper atoms may be treated as a diatomic molecule, the resulting two-hole problem having strong analogies with that of the H_2 molecule. In this approach, which we follow in this paper, the effects of the bridging acetate groups (Figure 1) are manifest in the ligand field splitting of the d orbitals in zeroth order and in the parameterization of the spin–orbit coupling constant λ.

The crystal structure of cupric acetate was to some extent anticipated by Bleaney and Bowers in their interpretation of the esr spectrum of the compound by their inclusion of a $-JS_1 \cdot S_2$ term in their spin Hamiltonian.[5] This term leads to a splitting J (an intrinsically negative integral with the dimensions of energy) between the spin singlet and triplet states, obtained from two electrons constrained to different orbitals, of *ca.* 280 cm^{-1} such that, in this model, the coupling is antiferromagnetic. It is readily shown that this treatment leads to the prediction that the magnetic susceptibility of the dimer will have a temperature variation given by eq 1.[5] The experimental data may be fitted to this equation indicating that the pattern of energy levels is, indeed, quite well represented by a ground-state singlet with a low-lying triplet which may be thermally populated. It should be noted that this equation is, strictly, applicable only to a gaseous system and is not dependent upon the explicit form of the orbital wave functions. In the crystal, as in solution, the magnetic centers of adjacent dimeric molecules are well separated and so the assumption of a gaseous system is not unrealistic, as there are no chemical bridges between the dimers.

$$\chi_M' = \frac{2g^2N\beta^2}{kT}\left(3 + \exp\left(\frac{-J}{kT}\right)\right)^{-1} + N\alpha \qquad (1)$$

The value of J in (1) is best obtained by susceptibility measurements (from the value of Θ, the Weiss constant). Commonly, an alternative expression, due to Figgis and Martin, may be used.[6] This states that $J \simeq -1.6 \cdot kT_N$ where T_N is the Néel temperature (J may also be obtained, less accurately, from the temperature variation of the esr spectrum).[5] It is found that if an experimental value of J is used in eq 1, then the g

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