The electronic absorptions observed were all intense charge-transfer type. Since the ligand lacks nonbonding or high-energy filled π-donor orbitals on the phosphorus, the absorptions in the cationic complexes are undoubtedly due to metal to ligand (M → L) type charge transfer from the occupied metal d orbitals to the empty d_π-acceptor orbitals on the donor atom. The similarity of ETPB with cyanide has already been noted; the linear $Au(CN)_2^-$ complex also has intense charge-transfer bands of the M → L type in the same energy region.[9] Even though the halide ligands in the AuLX complexes possess nonbonding and π-donor orbitals, ligand to metal (L → M) charge transfer is considered unlikely since the metal 5d orbitals are all filled and the empty 6s or 6p orbitals are of too high energy.

Although the structures of the complexes prepared here cannot be inferred from the spectral data, it is probable that the two-coordinate complexes AuLX, $AuL(CH_3CN)^+$, and AuL_2^+ are linear. Indeed linear two-coordination is common for gold(I). In contrast, four-coordinate complexes are not as common. Structural information is even more limited, but tetrahedral geometry about Au(I) is indicated in a few cases.[10] In addition, there are numerous examples of other d^{10} configuration metal ions which form four-coordinate tetrahedral complexes. Thus it is likely that AuL_4^+ has a tetrahedral structure. Its stability may be due in part to the low steric requirements of the ETPB ligand. The AuL_3^+ complex is probably also tetrahedral with a solvent molecule occupying the fourth coordination site; $AuL_3(CH_3CN)^+$ may be visualized as a solvolysis product of AuL_4^+.

Registry No. $[AuL(CH_3CN)]ClO_4$, 51240-04-1; $[AuL_2]ClO_4$, 51240-06-3; $[AuL_4]ClO_4$, 51240-08-5; AuLCl, 51240-09-6; AuLBr, 51240-10-9; $[(n\text{-}C_4H_9)_4N][AuCl_4]$, 17769-64-1; $[(n\text{-}C_4H_9)_4N][AuBr_4]$, 17769-65-2; $[Au(CH_3CN)_2]ClO_4$, 51240-11-0; $AuL_3(CH_3CN)^+$, 51240-35-8.

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Oxygen-17 Hyperfine Interactions in $ClOCl^+$, $FClO^+$, and Related Radicals

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Some uncertainty apparently persists[1] concerning the identity of the carriers of two epr spectra originally detected by Olah and Comisarow[2,3] and thought by them to be Cl_2^+ (I) and FCl^+ (II). Eachus, *et al.*, have suggested[4] the alternative formulations $ClOCl^+$ and $ClOF^+$ on the grounds that diatomic radicals in $^2\Pi_{3/2}$ states do not appear to be detectable in solution by the epr method. As triatomic, oxygen-containing species, these radicals would be isoelectronic with such well-established species as O_3^-, OClO, and FOO. However, some doubt was cast upon Eachus' suggestion by the failure of Gillespie and Morton to detect ^{17}O ($I = {}^5/_2$) hyperfine structure in a spectrum of II enhanced by the addition of enriched water.[5]

The magnitude of the ^{17}O hyperfine interaction (a_{17}) in these two radicals (should they prove, after all, to contain oxygen) is also important because of their close similarity to the peroxy radicals F_3COOO and FOO, whose ^{17}O hyperfine interactions[6,7] have never been positively assigned to specific oxygen nuclei.

For these reasons we decided to attempt a definitive identification of these radicals and determination of their ^{17}O hyperfine interaction constants (if any).

Results and Discussion

In order to minimize the viscosity of the medium, and hence to improve resolution of the spectra, ClF_3 was used as a solvent, rather than SbF_5 preferred by earlier workers. It was observed, however, that the addition of a small quantity of a Lewis acid such as AsF_5 greatly increased the intensity of the spectra obtained.

Radicals I and II are readily detectable in ClF_3-AsF_5 solutions unless precautions are taken to predry the vacuum line thoroughly with ClF_3. In fact, our procedure was to dry the system by flushing it with ClF_3 until a liquid sample of the latter yielded no epr spectrum on photolysis. We were then able to contaminate the ClF_3 with approximately 10 μmol of ^{17}O-enriched water, which enabled us to detect not only the spectra of radicals I and II but also the additional hyperfine structure associated with their ^{17}O analogs.

Radical I, identified by Olah and Comisarow[2] as Cl_2^+, has an ^{17}O hyperfine interaction of 20.6 G, and, since the two chlorine nuclei ($a_{35} = 2.25$ G) are equivalent, its identification as $ClOCl^+$ (symmetry C_{2v}, $^2B_1$) is confirmed. The second species, originally identified[3] as FCl^+, has an ^{17}O hyperfine interaction of 18.0 G. A comparison of its ^{35}Cl hyperfine interaction (12.9 G) with that of OClO (17.9 G), which we were also able to detect in ClF_3 as solvent, led us to prefer the formulation $FClO^+$ for radical II. We would expect the isomer $FOCl^+$ to have a considerably smaller ^{35}Cl hyperfine interaction, similar to that of $ClOCl^+$ (2.25 G).

In Table I data on the radicals $ClOCl^+$, $FClO^+$, and OClO observed in the present study are presented, together with data from other sources on related radicals.

Comparison with Other Radicals. Although Fessenden and Schuler determined the ^{17}O hyperfine constants (14.5, 22.2 G) of the radical FOO, they were unable to assign them unequivocally to the two positions.[7] Similarly, the three ^{17}O hyperfine interactions (3.6, 14.0, 23.3 G) in F_3COOO have not been assigned to specific nuclei,[6] although it may perhaps safely be assumed that the 3.6-G interaction belongs to the oxygen attached to the carbon atom.

However, from a comparison of the data on OClO and $FClO^+$, we note that replacing O^- by the more electronegative F causes the ^{17}O hyperfine interaction to increase markedly from 11.5 G in OClO to 18.0 G in $FClO^+$ and the ^{35}Cl interaction to decrease from 17.9 G (OClO) to 13.1 G ($FClO^+$). In performing the same substitution

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Table I. Epr Data for $ClOCl^+$, $FClO^+$, OClO, and Related Radicals

Radical	⟨g⟩	a_{17}, G	a_{19}, G	a_{35}, G	Ref
$ClOCl^+$	1.9986[a]	20.6[b]		2.25 (2)	*c*
$FClO^+$	2.0059	18.0	20.4	12.9	*c*
OClO	2.0100	11.5 (2)		17.9	*c*
FOO	2.0038	14.5	12.8		*d*
		22.2			
F_3COOO	2.0037	3.6	6.75		*e*
		14.0	0.55 (2)		
		23.3			
OOO^-	2.0096	10.5 (2)			*f*
		22.2			
$(H_3C)_3COO$	2.0146	23.4			*g*
		17.6			

[a] ±0.0002. [b] ±0.10 G. [c] This work. [d] Reference 6. [e] Reference 7. [f] S. Schlick, *J. Chem. Phys.*, 56, 654 (1972). [g] J. A. Howard, *Can. J. Chem.*, 50, 1981 (1972); K. Adamic, K. U. Ingold, and J. R. Morton, *J. Amer. Chem. Soc.*, 92, 922 (1970).

in O_3^-, we would therefore expect the hyperfine interaction of the terminal oxygen nucleus of FOO to be considerably larger than 10.5 G and that of its central oxygen to be rather smaller than 22.2 G, these being the respective isotropic interactions in O_3^- itself.[8] We therefore conclude that in FOO the larger (22.2 G) interaction is to be associated with the terminal oxygen nucleus, and the smaller (14.5 G) interaction is to be associated with the central oxygen. By analogy with FOO we conclude that in $F_3CO'''O''O'$ $a'_{17} = 23.3$ G, $a''_{17} = 14.0$ G, and $a'''_{17} = 3.6$ G.

A similar conclusion, later confirmed by Howard,[9] was reached by Adamic, *et al.*,[10] on the basis of line width variation across the ^{17}O hyperfine manifolds of the peroxy radical $(H_3C)_3COO$.

Experimental Section

The solvent, ClF_3 (Matheson), was handled in a copper vacuum line fitted with Whitey valves, Type 1VF4. The epr sample tubes were either Teflon FEP or Suprasil, 4-mm o.d. Arsenic pentafluoride (Allied Chemical) was used as a Lewis acid, and the ^{17}O source was water containing approximately 25 atom % ^{17}O (Yeda). In order to eliminate all traces of atmospheric moisture the entire vacuum system and the sample tubes were exposed to 0.5 atm of ClF_3 vapor for 0.5 hr. After reevacuation of the system approximately 50 μmol of AsF_5 and 10 μmol of enriched H_2O were dissolved in excess (approximately 200 μl) ClF_3. The samples could be photolyzed with a 1000-W Schoeffel Hg-Xe lamp; epr spectra were obtained with a Varian E-12 spectrometer equipped with a variable-temperature accessory. A CMC 707B frequency counter was used in conjunction with an HP540B transfer oscillator and Varian F-8A fluxmeter to measure the microwave frequency and magnetic field, respectively.

We found that if a sample of ClF_3 containing dissolved AsF_5 and water was photolyzed at −70°, a powerful signal due to $ClOCl^+$ could be detected. This signal disappeared rapidly on extinguishing the light. Use of water enriched in ^{17}O enabled us to determine a_{17} for this radical (20.6 G). The signal due to $FClO^+$ persisted for many hours after extinguishing the light and appeared to be optimized from the point of view of resolution of its hyperfine structure at −30°. Again, with the aid of ^{17}O-enriched water we were able to determine its a_{17} (18.0 G).

It may also be noteworthy that the epr spectrum of OClO appeared (without photolysis) in samples of ClF_3–AsF_5 to which several 10-μmol aliquots of water had been added. The ^{17}O hyperfine interaction was found to be 11.5 G, in excellent agreement with the value reported recently for OClO in toluene.[11]

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Registry No. $ClOCl^+$, 51174-96-0; $FClO^+$, 51174-97-1; OClO, 10049-04-4; ^{17}O, 13968-48-4.

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Mossbauer Effect in Oxygen-Bonded Antimony(III) Compounds. Aliphatic Esters and Oxobis(diphenylantimony)

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The effect of a group on the Mossbauer spectrum of a central metallic element can best be seen in a series of compounds with similar geometry. The ^{121}Sb Mossbauer effect has been studied in trivalent Sb(III) bonded to oxygen[2,3] and to carbon,[4,5] as well as other atoms. The several modifications of Sb_2O_3 are the only ones studied to date in the first category, as other inorganic oxides have more than three Sb–O bonds.[2b,3] In the present work we report results on a series of $Sb(OR)_3$ compounds, where R is an aliphatic group. The compound $[(C_6H_5)_2Sb]_2O$, oxobis[diphenylantimony(III)], which has both Sb–O and Sb–C bonds in the same molecule, has also been studied. Evidence that a Gol'danskii–Karyagin effect[6] does not occur in these compounds at 4°K has been obtained.

Experimental Section

Preparation and characterization of the $Sb(OR)_3$ compounds have been described elsewhere.[7] Because these are unstable when exposed to moist air, they were handled in a dry nitrogen atmosphere. Just prior to use, they were analyzed for Sb and agreement within at least 0.6 absolute per cent of the calculated percentage was taken as a criterion for lack of decomposition. The $[(C_6H_5)_2Sb]_2O$ was obtained from M & T Chemicals, Inc., Rahway, N. J., and was pure according to chemical analysis. *Anal.* Calcd for $[(C_6H_5)_2Sb]_2O$: Sb, 42.88; C, 50.7; H, 3.55. Found: Sb, 43.04; C, 50.2; H, 3.49.

The Mossbauer spectra were taken at liquid helium temperature as described earlier.[5] The $Sb(OR)_3$ compounds studied are liquids at room temperature, so absorbers were prepared by pouring the liquid onto polyethylene powder, quick-freezing in liquid nitrogen, and keeping the sealed holder cold until insertion into the cryostat. Because of the difficulty in handling these samples, the sample thickness has more error than for the $[(C_6H_5)_2Sb]_2O$ sample, a stable solid at room temperature.

Analysis of the spectra followed the procedure of Shenoy and Dunlap[8] with modifications to search for a Gol'danskii–Karyagin effect.[9] In the case of compounds with $\eta \approx 0$ this means allowing the $\Delta m = 1$ and $\Delta m = 0$ transition intensities to vary independently. For large η, m is no longer a valid quantum number. The ratio R_2/R_1,[9] corresponding to the intensity ratio $\Delta m = 0$ to $\Delta m = 1$ for $\eta = 0$, can still be determined. It proved unnecessary to invoke further

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