however, slight dissociation (<10%) was found for the most dilute samples used in the concentration study. It is assumed that these results are valid for $CH_2Cl_2$ solvent. The diffusion-limited second-order rate constant has been calculated using 8 ± 2 Å as the distance of closest approach and is $(3.2 \pm 0.7) \times 10^{10}$ l. $mol^{-1}$ $sec^{-1}$ at 25°.[18] The observed second-order rate constant is $(7.6 \pm 3.0) \times 10^8$ l. $mol^{-1}$ $sec^{-1}$ at 25°. These values suggest that electron transfer is not diffusion controlled especially when the tetramethylene derivative is considered in which case $k_2$ is at least another order of magnitude smaller. Studies under current investigation involve rate measurements for various counterions, solvents, and N substituents.

**Acknowledgments.** This research was supported by Grant GP-37795 from the National Science Foundation and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., and the University of Minnesota Graduate School.

**Registry No.** $Fe(Me_2dtc)_3$, 14484-64-1; $[Fe(Me_2dtc)_3]BF_4$, 35270-32-7.

[18] R. E. Weston, Jr., and H. A. Schwarz, "Chemical Kinetics," Prentice-Hall, Englewood Cliffs, N. J., 1972.

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Contribution from the Department of Chemistry,
Northern Illinois University, DeKalb, Illinois 60115

# Gold(I) Complexes of 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

Gerald P. Fenske, Jr.,[1] and W. Roy Mason*

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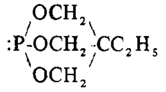
Gold(I) complexes of phosphorus donor ligands have long been of interest because the phosphorus donor stabilizes the univalent oxidation state, and such complexes are generally resistant to disproportionation to gold metal and Au(III) compounds.[2] In connection with studies of the electronic structure and reactivity of two-coordinate complexes, we have prepared several Au(I) complexes of the caged phosphite ligand[3] 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (ETPB), L. This ligand is of interest because its σ-donor and



L

π-acceptor abilities are similar to those of cyanide,[4] which forms an exceptionally stable two-coordinate complex of Au(I). In addition, L is virtually transparent in the uv spectral region and allows the observation of electronic absorptions of the complex unmasked by strong ligand absorptions.

A complex of Au(I) with a similar ligand, MTPB, with a 4-methyl substituent, was reported by Verkade and Piper[5] as a dinuclear complex $[AuL_2Cl]_2$. However, we were unable to prepare complexes of this stoichiometry. Instead in this note we report five complexes of ETPB, all of which are monomeric: $[AuL(CH_3CN)]ClO_4$, $[AuL_2]ClO_4$, $[AuL_4]ClO_4$, AuLCl, and AuLBr. The successive formation of the three cationic complexes was studied in acetonitrile, and their stabilities are discussed.

## Experimental Section

**Preparation of Compounds.** The gold compounds were prepared from either $[Au(CH_3CN)_2]ClO_4$[6] or $[(n\text{-}C_4H_9)_4N][AuX_4]$ (X = Cl, Br).[7] The ETPB ligand was obtained from Strem Chemicals, Inc., Danvers, Mass., and purified by distillation (mp 55-57°; lit.[8] mp 56°). *Anal.* Calcd for $C_6H_{11}O_3P$: C, 44.45; H, 6.84. Found: C, 44.2; H, 6.85. Acetonitrile was Spectro Grade and all other chemicals were of reagent grade. For the perchlorate salts, gold was determined spectrophotometrically as $Au(CN)_2^-$. An excess of cyanide ($CN^-$: Au > 5) was added to a known quantity of the salt dissolved in acetonitrile. The absorbance was measured at 41.9 kK and compared to that of a standard, $[(n\text{-}C_4H_9)_4N][Au(CN)_2]$,[9] using an absorptivity of 3888 $M^{-1}$ $cm^{-1}$. The precision of duplicate determinations was within 0.2%; the accuracy was within 1% of theory.

**Halo(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)gold(I), $Au(C_6H_{11}O_3P)X$.** A concentrated acetonitrile solution containing a 3-4 fold excess of ETPB was added slowly to a concentrated acetonitrile solution of $[(n\text{-}C_4H_9)_4N][AuX_4]$ (X = Cl, Br). Colorless solutions resulted and these were evaporated to a small volume and cooled in a Dry Ice-acetone slush bath. Colorless crystals were collected and washed with water. The solids were recrystallized from ethanol, washed with anhydrous ether, and dried *in vacuo* at room temperature overnight. Yield: AuLCl, 74%; AuLBr, 70%. *Anal.* Calcd for $Au(C_6H_{11}O_3P)Cl$: Au, 49.9; C, 18.26; H, 2.81; P, 7.85; Cl, 8.99. Found: Au, 49.2; C, 18.3; H, 2.82; P, 7.79; Cl, 8.90. Calcd for $Au(C_6H_{11}O_3P)Br$: Au, 44.9; C, 16.42; H, 2.53; P, 7.06; Br, 18.20. Found: Au, 44.2; C, 16.4; H, 2.57; P, 6.92; Br, 17.7.

**(Acetonitrile)(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)gold(I) Perchlorate, $[Au(C_6H_{11}O_3P)(CH_3CN)]ClO_4$.** A stoichiometric amount of ETPB in a concentrated acetonitrile solution was added slowly to $Au(CH_3CN)_2^+$ in acetonitrile solution. The addition of the ligand and subsequent isolation was performed in a dry nitrogen atmosphere. The resulting solution was evaporated to a small volume, cooled in a Dry Ice-acetone slush bath, and excess anhydrous ether was added. A gummy colorless precipitate remained after the ether-acetonitrile solution was decanted. The precipitate was washed with two additional portions of ether and dried *in vacuo* at room temperature for 2.5 hr. The white salt darkened on standing at room temperature and was analyzed immediately. It could be stored for a few days at −16° without apparent decomposition, however; yield 40%. *Anal.* Calcd for $[Au(C_6H_{11}O_3P)(CH_3CN)]ClO_4$: Au, 39.4; C, 19.23; H, 2.83; N, 2.80. Found: Au, 40.1; C, 19.0; H, 2.93; N, 2.62.

**Bis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)gold(I) Perchlorate, $[Au(C_6H_{11}O_3P)_2]ClO_4$.** A 2:1 stoichiometric amount of ETPB in a concentrated acetonitrile solution was added slowly under nitrogen to a solution of $Au(CH_3CN)_2^+$ in acetonitrile. The resulting solution was evaporated to a small volume and cooled in a Dry Ice-acetone slush bath. Anhydrous ether was added whereupon a pale yellow crystalline precipitate was formed. The precipitate was collected, washed with ether, and dried *in vacuo* at room temperature overnight; yield 60%. *Anal.* Calcd for $[Au(C_6H_{11}O_3P)_2]ClO_4$: Au, 31.7; C, 23.22; H, 3.57; P, 9.98. Found: Au, 31.1; C, 23.6; H, 3.78; P, 10.20.

**Tetrakis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)gold(I) Perchlorate, $[Au(C_6H_{11}O_3P)_4]ClO_4$.** A 10% excess of ETPB in a concentrated acetonitrile solution was added slowly under dry nitrogen to $Au(CH_3CN)_2^+$ in acetonitrile. Colorless crystals were formed on evaporating the resulting solution to a small volume and cooling in a Dry Ice-acetone slush bath. These crystals were collected, washed with anhydrous ether, and dried *in vacuo* at room tempera-

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[1] Abstracted in part from the M.S. thesis of G. P. F., Northern Illinois University, June 1974.

[2] See for example B. F. G. Johnson and R. Davis, "Comprehensive Inorganic Chemistry," A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, Chapter 29.

[3] For a review of this and related ligands see J. G. Verkade and K. J. Coskran, "Organic Phosphorus Compounds," Vol. 2, G. M. Kosolapoff and T. Maier, Ed., Wiley-Interscience, New York, N. Y., 1972, p 1; J. G. Verkade, *Coord. Chem. Rev.*, 9, 1 (1972).

[4] J. G. Verkade and T. S. Piper, *Inorg. Chem.*, 2, 944 (1963).

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[6] G. Bergerhoff, *Z. Anorg. Allg. Chem.*, 327, 139 (1964).

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[8] W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, 84, 610 (1962).

[9] W. R. Mason, *J. Amer. Chem. Soc.*, 95, 3573 (1973).

ture overnight; yield 51%. *Anal.* Calcd for $[Au(C_6H_{11}O_3P)_4]ClO_4$: Au, 20.85; C, 30.51; H, 4.69; P, 13.11. Found: Au, 20.78; C, 30.62; H, 4.53; P, 13.28.

**Formation Constants in Acetonitrile.** An estimate of the formation constant for $AuL_4^+$ from $AuL_3^+$ was made from absorbance *vs.* [L] data for acetonitrile solutions of $Au(CH_3CN)_2^+$ containing varying amounts of ETPB, all of which were greater than a 3:1 stoichiometric amount. The formation constant $K_4$ was calculated from eq 1, where $A$ is the measured absorbance, $A_3$ is the absorbance due

$$K_4 = (A_3 - A)/(A - A_4)\{[L]_0 - [3 + (A_3 - A)/(A_3 - A_4)][Au]_0\} \tag{1}$$

to $AuL_3^+$, and $A_4$ is the absorbance due to $AuL_4^+$, each at 42.6 kK (the absorbance due to uncomplexed ligand was negligible at this energy); $[L]_0$ and $[Au]_0$ are the total ligand and gold concentrations, respectively. The derivation of eq 1 assumes the L:Au ratio is >3 and that $AuL_3^+$ and $AuL_4^+$ are the only gold complexes present. Values of $K_4$ calculated for the nine different concentrations of ETPB were self-consistent to within ±5%.

## Results and Discussion

The five ETPB complexes were each analyzed and characterized by electronic and infrared spectra. Figure 1 presents the electronic spectra for the cationic complexes in acetonitrile. Spectral data are collected in Table I.

Table I. Infrared and Electronic Spectral Data

| Complex | Ir absorption bands, $\bar{\nu}$, cm$^{-1}$ [a] |
|---|---|
| $[AuL(CH_3CN)]ClO_4$ [b] | 2370 m, b, 1160 w, 1020 m, b, (950 m, b), (850 w), 832 m, 652 m, 545 w |
| $[AuL_2]ClO_4$ [b] | 1160 w, 1030 s, 952 s (850 s), 837 s, 645 m, 535 w |
| $[AuL_4]ClO_4$ [b] | 1158 m, b, 1028 s, b, 948 s, 850 m, 808 m, (778 w), 642 m, 530 w |
| AuLCl [c] | 2980 m, 1470 w, b, 1404 w, b, (1190 w), 1158 m, 1042 s, 956 s, (852 s), 837 s, 658 m, 548 w, b |
| AuLBr [b] | 1190 w, 1155 m, 1030 s, (960 w), (848 s), 823 s, (805 s), 653 m, 546 w |
| L = ETPB [b] | 2975 s, b, 1480 m, b, 1408 m, (1190 w), 1158 m, 1052 s, 963 s, 855 m, (784 s), 745 s, 650 m, 530 w |

| Complex | Electronic absorption bands, $\bar{\nu}$, kK ($\epsilon$, $M^{-1}$ cm$^{-1}$) [d] |
|---|---|
| $[Au(CH_3CN)_2]ClO_4$ | 46.65 (4040), 50.3 (4920) |
| $[AuL(CH_3CN)]ClO_4$ | 43.05 (2050), 44.75 (3120), 50.75 (12,070) |
| $[AuL_2]ClO_4$ | 40.8 (1370),[e] 42.5 (3240), 49.25 (18,620) |
| $[AuL_4]ClO_4$ | 50.0 (19,290)[e] |
| AuLCl | 43.75 (2720), 44.75 (2180),[e] 47.5 (3000),[e] 50.0 (7180)[e] |
| AuLBr | 43.8 (3200), 45.2 (3140) |

[a] Beckman IR-12. Key: s, strong; m, medium; w, weak; b, broad; shoulder absorption indicated by parentheses; absorptions due to perchlorate not included. [b] Nujol mull on CsI plates. [c] KBr pellet. [d] Cary Model 1501; acetonitrile solutions. [e] Shoulder; $\epsilon$ is for the value of $\bar{\nu}$ given.

Table II. Formation Constants for $AuL_4^+$ in Acetonitrile at 25°

| $10^3[L]_0$, $M$ | $A$(42.6 kK) | $10^{-3}$ $K_4$,[a] $M^{-1}$ | $10^3[L]_0$, $M$ | $A$(42.6 kK) | | $10^{-3}K_4$,[a] $M^{-1}$ |
|---|---|---|---|---|---|---|
| 1.586 | 0.804 | 6.6 | 2.324 | 0.277 | | 6.9 |
| 1.682 | 0.693 | 6.4 | 2.571 | 0.223 | | 6.9 |
| 1.778 | 0.596 | 6.3 | 3.077 | 0.172 | | 6.5 |
| 1.914 | 0.482 | 6.4 | 2.938 | 0.617 | | 6.6[b] |
| 2.051 | 0.394 | 6.4 | | | Av | 6.6 ± 0.2 |

[a] $K_4 = [AuL_4^+]/([AuL_3^+][L])$. $[Au(I)] = 4.91 \times 10^{-4}$ $M$; $\epsilon_{42.6\ kK}(AuL_3^+) = 1940$ $M^{-1}$ cm$^{-1}$; $\epsilon_{42.6\ kK}(AuL_4^+) = 143$ $M^{-1}$ cm$^{-1}$. [b] $[Au(I)] = 7.44 \times 10^{-4}$ $M$.

In order to investigate the successive formation of the cationic complexes from $Au(CH_3CN)_2^+$ and ETPB in acetonitrile, electronic spectra were obtained for various L:Au ratios. With the Au(I) concentration fixed and the L:Au ratio varied between 0 and 1.00, an isosbestic point was observed at 45.1 kK between $Au(CH_3CN)_2^+$ and $AuL(CH_3CN)^+$. Similarly, for L:Au between 1.00 and 2.00, isosbestic points were observed at 42.9 and 44.9 kK between $AuL(CH_3CN)^+$ and $AuL_2^+$. The spectra at L:Au = 1.00 and 2.00 were identical with those measured for isolated $[AuL(CH_3CN)]ClO_4$ and $[AuL_2]ClO_4$ salts, and the isosbestic points agreed within experimental error with those predicted from a comparison of their spectra (Figure 1). For L:Au ratios between 2.00 and 3.00, a very weak isosbestic point at 38.6 kK was noted, but this point disappeared for L:Au > 3, and a new point was found at 43.4 kK. Furthermore, the spectra obtained at L:Au ≧ 8 were identical with spectra measured for $[AuL_4]ClO_4$ in the presence of the same excess ligand. Mole ratio plots were constructed covering L:Au ratios from 0 to 8. Figure 2 illustrates such a plot. Four regions can be distinguished in these plots: L:Au between 0 and 1.00, between 1.00 and 2.00, between 2.00 and 3.00, and above 3.00. These four regions, together with the isosbestic points observed, are consistent with eq 2-5 describing the successive

$$Au(CH_3CN)_2^+ + L \overset{K_1}{\rightleftharpoons} AuL(CH_3CN)^+ + CH_3CN \tag{2}$$

$$AuL(CH_3CN)^+ + L \overset{K_2}{\rightleftharpoons} AuL_2^+ + CH_3CN \tag{3}$$

$$AuL_2^+ + L \overset{K_3}{\rightleftharpoons} AuL_3^+ \tag{4}$$

$$AuL_3^+ + L \overset{K_4}{\rightleftharpoons} AuL_4^+ \tag{5}$$

addition of L to the Au(I) coordination sphere. Unfortunately the $AuL_3^+$ complex was not isolated, but the isosbestic behavior provides evidence for its existence. No isosbestic behavior is predicted below 49 kK for $AuL_2^+$ and $AuL_4^+$. The existence of a well-defined point at 43.4 kK for L:Au ≧ 3.00 indicates the presence of an intermediate complex between $AuL_2^+$ and $AuL_4^+$ and that this complex is transformed into $AuL_4^+$ in the presence of excess ligand. The sharp breaks in the curve in Figure 2 at L:Au = 1.00 and 2.00 indicate that $K_1$ and $K_2$ are both very large. Further, since only $AuL(CH_3CN)^+$ is formed up to L:Au = 1.00, $K_1$ must be significantly larger than $K_2$; similarly since only $AuL_2^+$ is formed up to L:Au = 2.00, $K_2$ must be larger than $K_3$. The plot in Figure 2 (and others constructed at different energies) between L:Au = 2.00 and 3.00 is very nearly linear in contrast to the marked curvature at L:Au above 3. This suggests that $K_3$ is larger than $K_4$. The value of $K_4$ can be estimated from absorbance *vs.* [L] data assuming reasonable values for the absorbances of $AuL_3^+$ and $AuL_4^+$. Values of $K_4$ calculated from eq 1 are tabulated in Table II. The self-consistency obtained is encouraging and lends support to the interpretation of the data for L:Au above 3. Attempts to fit the data to a conversion of $AuL_2^+$ to $AuL_4^+$ by the addition of 2 mol of L were not successful. The solid curve in Figure 2 was plotted for a value of $K_4 = 6.6 \times 10^3$ $M^{-1}$. Thus the normal order of stepwise constants, $K_1 > K_2 > K_3 > K_4$, is consistent with our observations.

When $[AuL_4]ClO_4$ is dissolved in acetonitrile in the absence of excess ligand, absorption bands are observed which are identical in energy with spectra obtained for solutions of $Au(CH_3CN)_2^+$ and ETPB with L:Au = 3.00. On addition of excess ligand, these bands are suppressed. Beer's law does not hold for the $AuL_4^+$ complex in the absence of added ligand. Using the value of $K_4$, the $AuL_4^+$ complex is predicted

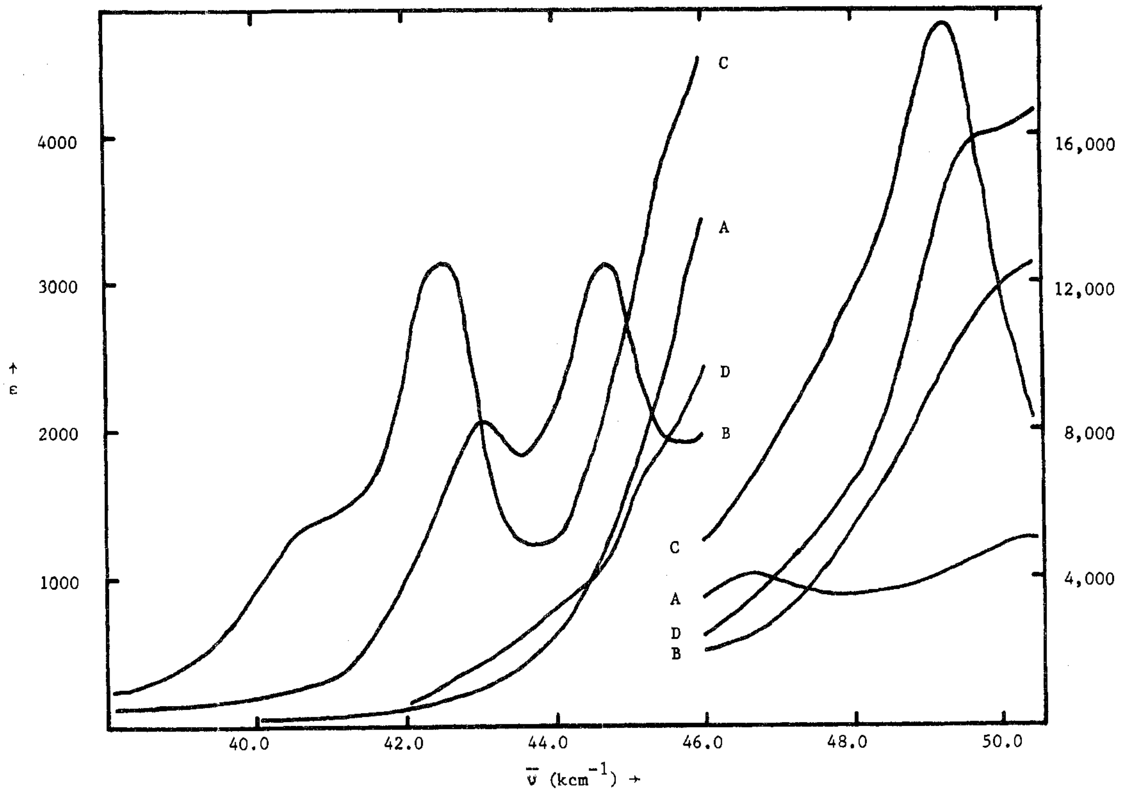

Figure 1. Electronic spectra of cationic Au(I) complexes in acetonitrile: A, $[Au(CH_3CN)_2]ClO_4$; B, $[AuL(CH_3CN)]ClO_4$; C, $[AuL_2]ClO_4$; D, $[AuL_4]ClO_4$.

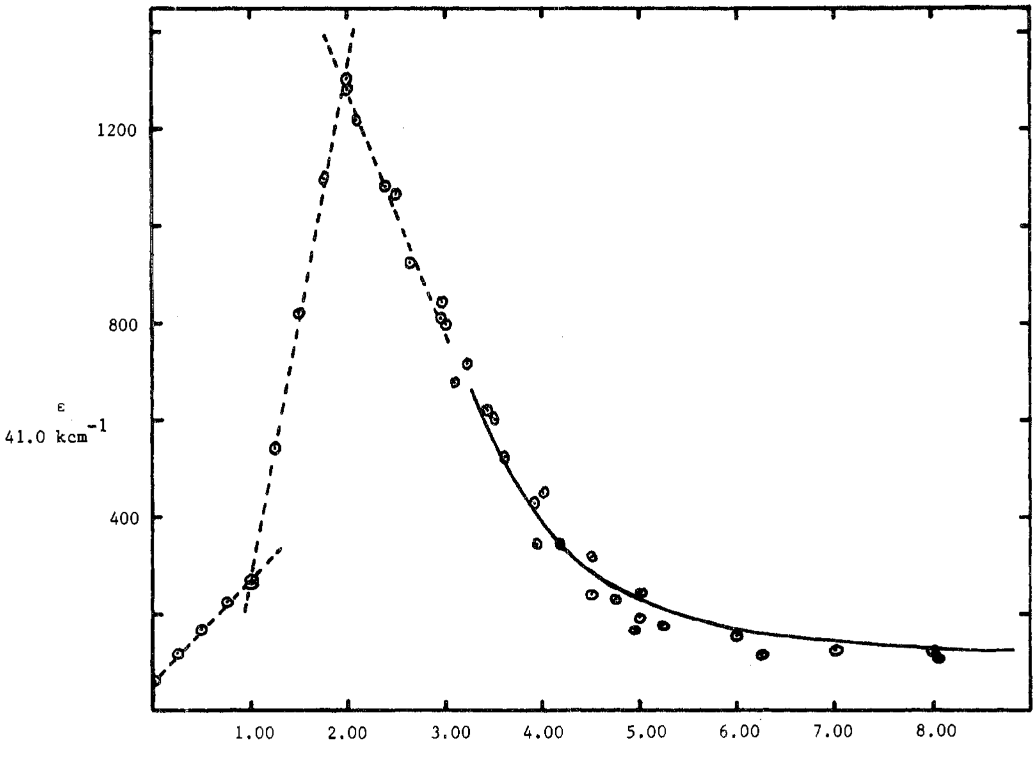

Figure 2. Mole ratio plot constructed from data collected at 41.0 kK. The solid line was determined for $K_4 = 6.6 \times 10^3 M^{-1}$ and $[Au(I)] = 5 \times 10^{-4} M$. The experimental points were determined for $[Au(I)] = (4.9\text{–}7.4) \times 10^{-4} M$.

to be about 42% dissociated for $[Au(I)] = 5 \times 10^{-4} M$. The failure of Beer's law can be explained since the degree of dissociation will depend upon the gold concentration.

The infrared spectra of all the ETPB complexes showed ligand absorptions which were only slightly shifted on coordination from those of the free ligand. Some evidence for a C-N stretching band appears near 2370 cm$^{-1}$ for $AuL(CH_3CN)^+$, though the absorption was weak.

The electronic absorptions observed were all intense charge-transfer type. Since the ligand lacks nonbonding or high-energy filled $\pi$-donor orbitals on the phosphorus, the absorptions in the cationic complexes are undoubtedly due to metal to ligand ($M \rightarrow L$) type charge transfer from the occupied metal d orbitals to the empty $d_\pi$-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 $M \rightarrow L$ type in the same energy region.[9] Even though the halide ligands in the AuLX complexes possess nonbonding and $\pi$-donor orbitals, ligand to metal ($L \rightarrow M$) 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.

(10) W. Cohran, F. A. Hart, and F. G. Mann, *J. Chem. Soc.*, 2816 (1957).

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Contribution No. 13964 from the Division of Chemistry, National Research Council Canada, Ottawa, Canada

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

J. R. Morton* and K. F. Preston

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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 $\mu$mol 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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