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DIRECT SYNTHESIS USING GOLD ATOMS: SYNTHESIS, INFRARED AND ULTRAVIOLET-VISIBLE SPECTRA AND MOLECULAR ORBITAL INVESTIGATIONS OF MONOETHYLENE GOLD(0), $(C_2H_4)Au$

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Summary

The reaction of Au atoms with $^{12}C_2H_4$ or $^{12}C_2H_4/Ar$ mixtures at 8—10 K yields a single product. Using Au and $^{12}C_2H_4$ concentration experiments, warm-up studies and $^{13}C_2H_4/Ar$, $^{12}C_2H_4/^{13}C_2H_4/Ar$ isotopic substitution, coupled with infrared and UV-visible spectroscopy, the product is characterized to be monoethylene gold(0), $(C_2H_4)Au$, the first reported example of a zerovalent gold-olefin complex. Extended Hückel molecular orbital calculations proved to be a useful aid towards the assignment of the optical spectrum of $(C_2H_4)Au$. The thermal stability of $(C_2H_4)Au$ in solid C_2H_4 at 70 K is discussed in terms of the feasibility of a macroscale, liquid nitrogen temperature, chemical synthesis. The molecular and electronic properties of the group of complexes $(C_2H_4)M$ and $M(O_2)$, where M = Ag or Au, are compared and discussed.

Introduction

The olefin gold compounds which have been prepared and characterized to date [1] may be classified as being on the one hand monomeric adducts of gold(I) chloride and on the other binuclear mixed complexes containing both gold(I) and gold(III). Prior to this study, however, olefin complexes of zerovalent gold were unknown although ethylene does chemisorb onto gold films [2].

In view of our recent synthesis and spectroscopic characterization of binary ethylene complexes of zerovalent copper [3], $(C_2H_4)_nCu$ (where n = 1—3), and silver [4], $(C_2H_4)Ag$, from copper atom, silver atom-ethylene cocondensation reactions, it was thought to be of considerable chemical interest to establish the reactivity pattern of gold atoms with ethylene under similar cryogenic conditions.

In practice, the Au/C_2H_4 cocondensation reaction yields only monoethylene gold(0) irrespective of whether pure ethylene or dilute ethylene—inert gas matrices are used. The following is a detailed account of our experimental and theoretical investigations with this new system.

Experimental

Monatomic gold was generated by either directly heating a thin tungsten rod (0.025") around the center of which was wound gold wire (0.005") or by directly heating a tantalum Knudsen cell (wall thickness 0.015", orifice diameter 0.010—0.020"), the gold being contained in a boron nitride liner (wall thickness 0.005"). The gold metal (99.99%) was supplied by Imperial Smelting Company, Toronto. Research grade $^{12}C_2H_4$ (99.90%) was supplied by Matheson of Canada and $^{13}C_2H_4$ (90%) by Stohler Isotopes, Montreal. The furnace used for the evaporation of the metals has been described previously [5]. The rate of gold atom deposition was continuously monitored using a quartz crystal microbalance [6]. In the infrared experiments, matrices were deposited on either a NaCl or CsI plate cooled to 10 K by means of an Air Products Displex closed-cycle helium refrigerator. Infrared spectra were recorded on a Perkin—Elmer 180 spectrophotometer. UV-visible spectra were recorded on a standard Varian Techtron instrument in the range 190—900 nm, the sample being deposited on a NaCl optical plate. Extended Hückel molecular orbital calculations were run on an IBM 370 computer.

Infrared experiments

When Au vapor (which is known to be greater than 99% atomic under the conditions of our experiment [7] is cocondensed with $^{12}C_2H_4/Ar \simeq 1 : 10$ at 8—10 K (using low concentrations of Au to eliminate complications due to cluster formation [8], $Au/C_2H_4 \simeq 10^{-4}$), a yellowish-green matrix is obtained I, the infrared spectrum of which is shown in Fig. 1 (B). Aside from absorptions attributable to free ethylene (labelled E), major new lines are observed at 3053w, 1476mw, 1144s, 890w cm^{-1} which are characteristic of coordinated ethylene. Decreasing the $^{12}C_2H_4/Ar$ ratio to 1 : 100 (Fig. 1 (A)) produced no evidence for any other species besides the one formed in concentrated $^{12}C_2H_4/Ar$ (Fig. 1 (B)), the gross features of the infrared spectrum remaining essentially unchanged (Table 1). Moreover, when Au atoms are cocondensed with pure C_2H_4 (Fig. 1 (C)) the same yellowish-green compound (I) is formed as evidenced by the extremely close correspondence of its infrared absorptions to those observed in concentrated and dilute $^{12}C_2H_4/Ar$ matrices (Fig. 1 (A,B), and Table 1).

Furthermore, warming the $^{12}C_2H_4/Ar$ matrices from 10—40 K simply caused a diminution of the absorbances of all of the infrared lines assigned to I at roughly the same rate, thereby reinforcing the view that they may be ascribed to a single absorbing species.

The ethylene concentration studies and the warm-up experiments for compound I, when taken in conjunction with the remarkably close resemblance of its infrared spectrum to those reported for $(C_2H_4)Cu$ [3] and $(C_2H_4)Ag$ [4] (Table 2), strongly suggest that I is best formulated as monoethylene gold(0), $(C_2H_4)Au$.

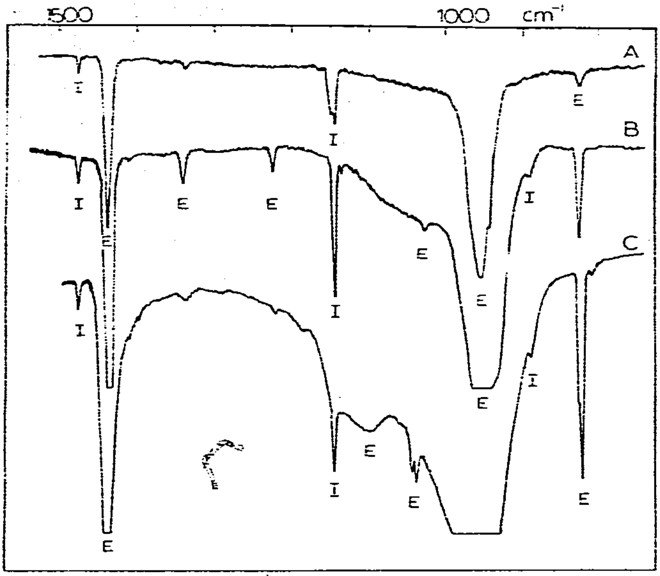

Fig. 1. The matrix infrared spectrum of the product of the Au atom (A) $^{12}C_2H_4/Ar \simeq 1:100$ (B) $^{12}C_2H_4/Ar \simeq 1:10$ and (C) $^{12}C_2H_4$ reaction at 8—10 K showing the exclusive formation of $(C_2H_4)Au$ labelled I. Infrared absorptions associated with free $^{12}C_2H_4$ in the matrix are labelled E.

Other sources of experimental data which support this assignment stem from $^{12}C_2H_4/^{13}C_2H_4/Ar$ mixed isotopic substitution, UV-visible spectroscopy and extended Hückel molecular orbital calculations to be described.

Infrared experiments with $^{12}C_2H_4/^{13}C_2H_4/Ar$ isotopic mixtures

To make an unequivocal stoichiometric assignment for compound I, mixed isotopic data (preferably involving ^{13}C-labelled ethylene rather than D-labelling, to minimize H/D scrambling effects of the type experienced with $Ag/C_2H_4/C_2D_4/Ar$ mixtures [9]) for at least one of the characteristic modes of the coordinated ethylene are required. In this context, $^{12}C_2H_4/^{13}C_2H_4/Ar \simeq 1:1:10$ mixtures favored optimum spectral resolution conditions and the $\nu(^{12}C{=}^{12}C)$ stretching (1475 cm^{-1}) and $\delta(^{12}CH_2)$ deformational (1144 cm^{-1}) modes, although expected to be extensively coupled [13], proved to be the most suit-

TABLE 1

THE Au/C_2H_4 COCONDENSATION REACTION; INFRARED DATA

C_2H_4 (pure)	C_2H_4/Ar (1 : 10)	C_2H_4/Ar (1 : 100)	Approximate description of mode
3048w ^{a}	3053w ^{a}	^{a,b}	$\nu(CH_2)$
1474mw	1476mw	1475mw	$\left.\begin{matrix}\nu(CC)\\ \delta(CH_2)\end{matrix}\right\}^c$
1144s	$\left.\begin{matrix}1144s\\ 1135vvw\end{matrix}\right\}$	$\left.\begin{matrix}1158s\\ 1154mw(sh)\end{matrix}\right\}$	
889w	890w	^{b}	$\rho_w(CH_2)$

^{a} Partially overlapped by the $\nu(CH_2)$ absorptions of free C_2H_4 in the matrix. ^{b} Too weak to observe under high dilution conditions. ^{c} These modes are expected to be extensively mixed (see ref. 13).

TABLE 2

INFRARED SPECTRA FOR $(C_2H_4)M$, WHERE M = Cu, Ag, Au

$(C_2H_4)Cu$ (ref. 3)	$(C_2H_4)Ag$ (ref. 4)	$(C_2H_4)Au$ (this study)	Approximate description of mode
1475	1476	1476	$\nu(CC)$
1164	1152	1144	$\delta(CH_2)$
1155	1132	1135	
840	794	890	$\rho_w(CH_2)$

able for studying isotopic structure. For example, when $^{13}C_2H_4/Ar \simeq 1:10$ mixtures were used, the corresponding $\nu(^{13}C{=}^{13}C)$ stretching and $\delta(^{13}CH_2)$ deformational modes of compound I were observed at 1452 and 1124 cm^{-1}, respectively (Table 3). However, when $^{12}C_2H_4/^{13}C_2H_4/Ar \simeq 1:1:10$ mixtures were used the resulting infrared spectrum of compound I was simply a superposition of the absorptions observed in the isotopically pure runs, $^{12}C_2H_4/Ar$ and $^{13}C_2H_4/Ar$, respectively (Table 3). No other isotopic lines were observed between those of the $\nu(C{=}C)$ stretching modes at 1476—1452 cm^{-1} or the $\delta(CH_2)$ deformational modes, 1144/1124 cm^{-1} (Table 3), as would be expected for a $(C_2H_4)_nAu$ complex with n greater than one. On the basis of these isotopic data, compound I can be confidently assigned to monoethylene gold(0), in line with our earlier discussions *.

Ultraviolet-visible experiments

To ensure reproducible conditions, infrared and UV-visible spectra were recorded consecutively from the same $(C_2H_4)Au$ sample in $C_2H_4/Ar \simeq 1:10$ matrices. A typical trace is shown in Fig. 2 (B) together with the corresponding

TABLE 3

$^{12}C_2H_4/^{13}C_2H_4$ ISOTOPIC DATA FOR MONOETHYLENE GOLD(0)

$^{12}C_2H_4/Ar$ (1 : 10)	$^{13}C_2H_4/Ar$ (1 : 10)	$^{13}C_2H_4/^{13}C_2H_4/Ar$ (1 : 1 : 10)	Assignment
1476		1476	$\nu(^{12}C{=}^{12}C)$
	1452	1452	$\nu(^{13}C{=}^{13}C)$
1144		1144	$\delta(^{12}CH_2)$ [a]
	1124	1124	$\delta(^{13}CH_2)$

[a] The $\delta(CH_2)$ deformational mode is particularly sensitive to the temperature of deposition and appears to display a multiple trapping site effect. For example, 8—10 K depositions show just the 1144 cm^{-1} (site I_1) mode. However 10—15 K depositions enhance a second site as seen by the appearance of $\delta(CH_2)$ mode at 1113 cm^{-1} (site I_2). A multiple trapping site assignment is favoured on the basis of the $^{12}C_2H_4/^{13}C_2H_4/Ar$ experiments which simply show the 1144/1124 cm^{-1} (site I_1) doublet together with a corresponding 1113/1092 cm^{-1} (site I_2) doublet.

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* In the event of extremely weak coupling between the vibrational modes of coordinated ethylene ligands in a $(C_2H_4)_nM$ complex (where $n > 1$) one might not be able to resolve the isotopic components of the $^{12}C_2H_4/^{13}C_2H_4$ mixed isotopic molecules and one could be mislead into believing that one was dealing with a monoethylene, rather than a higher stoichiometry ethylene complex. However, in view of our detailed $Au/C_2H_4/Ar$ concentration studies which show the formation of just a single species, we are confident that our monoethylene gold formulation is correct.

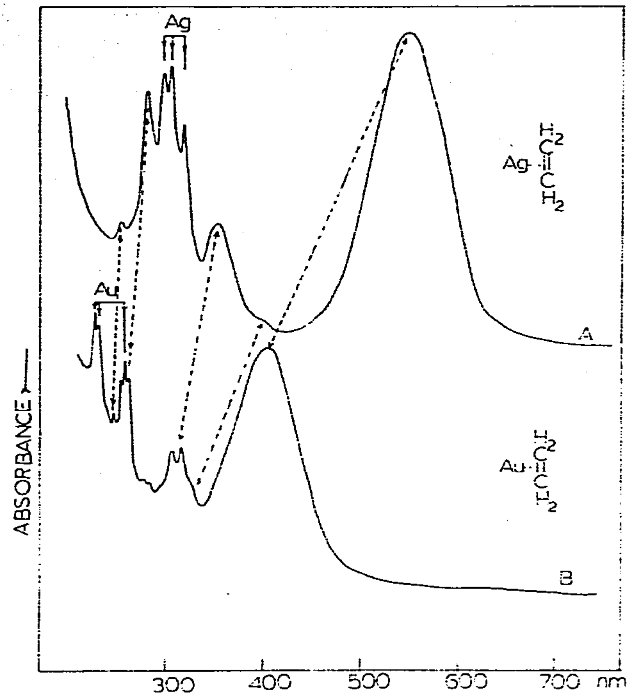


Fig. 2. The UV-visible spectrum of (A) $(C_2H_4)Ag$ and (B) $(C_2H_4)Au$ in $^{12}C_2H_4/Ar \simeq 1:10$ matrices at 8—10 K. Lines ascribed to trace amounts of Ag and Au atoms are indicated with arrows.

data for $(C_2H_4)Ag$ for the purposes of comparison (Fig. 2 (A)). Apart from the presence of three sharp absorptions attributable to small amounts of unreacted Au and Ag atoms isolated in the Ar matrices, the electronic spectra of $(C_2H_4)Au$ and $(C_2H_4)Ag$ are very similar (Fig. 2 (A,B)). A blue shift is observed for all absorptions on passing from $(C_2H_4)Ag$ to $(C_2H_4)Au$ (Table 4).

The electronic spectra of $(C_2H_4)Au$ and $(C_2H_4)Ag$ are dominated by intense, broad absorptions centered at roughly 401 nm and 550 nm, respectively, and are presumably responsible for the yellowish-green and purple colors of the compounds.

TABLE 4

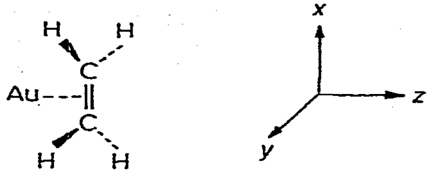
THE UV-VISIBLE SPECTRA OF MONOETHYLENE GOLD(0) AND MONOETHYLENE SILVER(0) IN $^{12}C_2H_4/Ar = 1:10$ MATRICES

$(C_2H_4)Au$ (this study)	$(C_2H_4)Ag$ (ref. 4)
401s(br) [a]	550s(br) [b]
327w(sh)	404vw(sh)
315 304	355m
261m 252m	283ms
246vw	253vw

[a] $\Delta\nu_{1/2} \simeq 4300$ cm^{-1}. [b] $\Delta\nu_{1/2} \simeq 3060$ cm^{-1}.

Extended Hückel molecular orbital calculations for (C_2H_4)Au

In an effort to obtain an insight into the electronic structure of monoethylene gold(0) we have performed extended Hückel molecular calculations on the complex with the C_{2v} geometry shown below:



The basis set of valence atomic orbitals for Au consisted of 5*d*, 6*s* and 6*p* and the various orbital exponents and H_{ii} values were taken from the work of Baetzold [10] (Table 5). The carbon and hydrogen parameters of Hoffmann et al. [11a], Skinner et al. [11b] and Richardson et al. [11c] were used for the ethylene moiety (Table 5).

The molecular orbital energy level scheme that results from these calculations is shown in Fig. 3. In line with the Dewar—Chatt—Duncanson [12] scheme of metal—olefin bonding, one finds that the main bonding interactions between the ethylene and gold are through a_1 (σ) and b_1 (π) molecular orbitals which are best described as [Au ($6s5d_{z^2}$) + C_2H_4 (π_u)] and [Au ($5d_{xz}$) + C_2H_4 (π_g)] combinations. The gold atomic orbitals $5d_{x^2-y^2}$, $5d_{xy}$, $5d_{z^2}$ and $5d_{yz}$ remain essentially non-bonding in this scheme, around —11 eV. The unpaired electron of (C_2H_4)Au resides in a $b_1(\pi^*)$ type molecular orbital which is best described as a [Au($6p_x5d_{xz}$) — C_2H_4 (π_g)] antibonding combination, resulting in a $^2B_1$ electronic ground state for (C_2H_4)Au.

Assuming that our molecular orbital description of (C_2H_4)Au is qualitatively correct, then it would not seem unreasonable to describe the visible absorption at 401 nm as a Au → C_2H_4 charge transfer transition originating from electric dipole and spin-allowed electronic transitions, localized mainly between the group of Au 5*d* orbitals (centered around —11 eV) and the partially-filled b_1 (π^*) level at about —8.7 eV.

The origin of the remaining high energy absorptions is less certain although

TABLE 5

PARAMETERS [a] USED IN THE EHMO CALCULATIONS OF MONOETHYLENE GOLD(0)

	Orbital	Orbital exponent	H_{ii} (eV) [b]
Au [10]	5*d*	4.025	—11.09
	6*s*	1.823	—9.22
	6*p*	1.823	—4.37
C [11a]	2*s*	1.625	—21.40
	2*p*	1.625	—11.40
H [11a]	1*s*	1.000	—13.60

[a] Bond lengths used were r(AuC) = 2.37 Å; r(CC) = 1.40 Å; r(CH) = 1.01 Å. [b] The C and H VOIP's of Skinner et al. [11b] and orbital exponents of Richardson [11c] were also tried in conjunction with the Cusach's approximation [16] for the calculation of the H_{ij} terms and produced essentially the same molecular orbital and bonding schemes for (C_2H_4)Au as described in the text and depicted in Fig. 3.

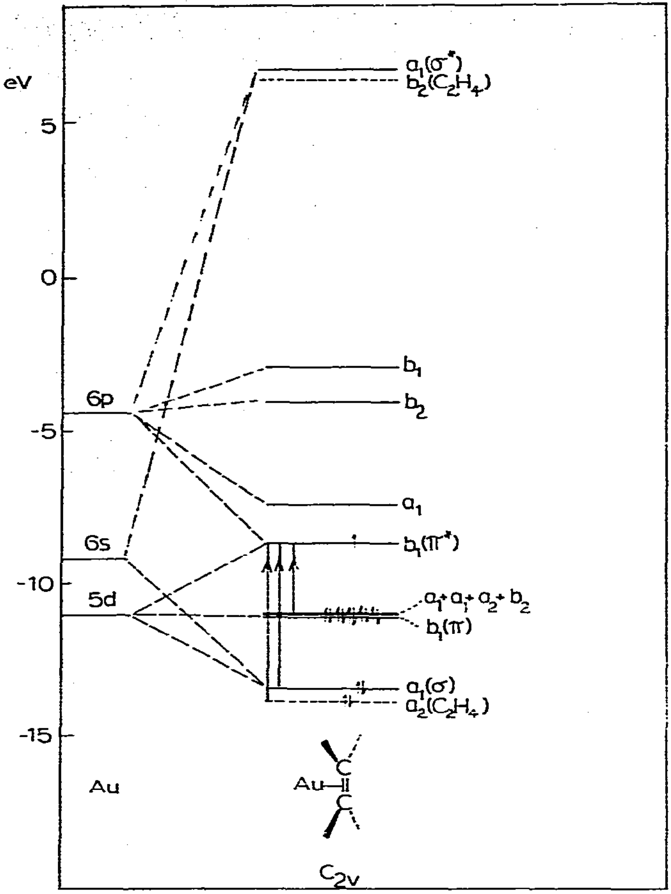


Fig. 3. The molecular orbital energy level scheme for $(C_2H_4)Au$ calculated using the extended Hückel approximation (see text for parameters and notation used).

it seems likely that they are associated with electronic transitions between low-lying orbitals and the partially-filled antibonding b_1 (π^*) level as illustrated schematically in Fig. 3.

While these calculations are qualitativley useful in gaining an insight into the bonding and the distribution of electronic levels in $(C_2H_4)Au$, we realize that the absolute transition energies are not really meaningful and clarification of the details of the electronic spectrum of $(C_2H_4)Au$ will require more sophisticated quantum mechanical calculations than those employed in the present study.

Discussion

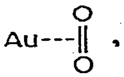
Being the first reported example of a zerovalent gold-olefin complex, certain properties of monoethylene gold(0) deserve special mention.

To begin with, the thermal stability and possible usefulness of $(C_2H_4)Au$ as a reagent for further organogold chemistry is of considerable interest. Our most optimistic observations along these lines stem from warm-up experiments in pure C_2H_4 matrices, which show the presence of unchanged $(C_2H_4)Au$ up to about 70 K, at which temperature the C_2H_4 is beginning to sublime off the optical plate. Whether or not the $(C_2H_4)Au$ complex decomposes at this temperature or alternatively is carried into the gas phase unchanged, together with the matrix support, cannot be established in this study. What is certain, however, is the likelihood of failure of a macroscale, liquid nitrogen temperature synthesis of $(C_2H_4)Au$ from Au atoms and C_2H_4 on the grounds that $(C_2H_4)Au$ could only be generated below 20 K. Between 20 K and 60 K, greyish-colored matrices were obtained which showed no infrared spectroscopic evidence for $(C_2H_4)Au$. This observation would indicate a marked preference for gold clustering rather than complex formation.

Another point of some interest relates to the striking similarity of the infrared spectroscopic data of $(C_2H_4)M$, where M = Cu, Ag or Au (Table 2), particularly in the 1500—1000 cm^{-1} region. If one used these wavenumber data as indicative of the extent of the metal-olefin interaction, one would be forced to conclude that the monoethylene complexes of the zerovalent Group IB complexes have comparable bonding properties and presumably similar thermal stabilities. However, deductions of this type are known to be fraught with difficulty, owing to the extensive vibrational coupling between the normal modes involving $\nu(C{=}C)$ stretching and $\delta(CH_2)$ symmetrical deformation [13]. In order to determine a realistic force field for molecules such as $(C_2H_4)M$, with the ultimate aim of evaluating changes in the C=C bond strength of ethylene on complexation and hence an insight into the metal—ethylene σ/π bonding interaction, a complete normal coordinate analysis is necessary. However, the paucity of vibrational modes observed in the present study of $(C_2H_4)Au$ rendered such an analysis meaningless. Further investigations along these lines will have to await the acquisition of a more complete set of vibrational data.

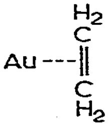
Although the infrared spectra for these monoethylene complexes in the region 3200—600 cm^{-1} appear to be insensitive to the central metal atom, this is not the case for their UV-visible spectra. For example, substantial frequency shifts are observed on passing from $(C_2H_4)Au$ to $(C_2H_4)Ag$ (Fig. 2 (A,B)) which are likely to be related to differences in the extent of the σ/π metal—ethylene bonding interactions. In particular, the major visible absorption frequency may prove to be a measure of the extent of metal → ethylene π-charge transfer, in which case one might expect $(C_2H_4)Au$ to be thermally more stable than $(C_2H_4)Ag$. This would appear to be the situation in practice although further investigations with other olefins will be required to explore these ideas.

A final and most intriguing observation relates to the striking similarity between the electronic spectra of:



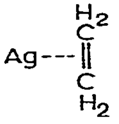
$$\mathrm{Au}\cdots\left(\begin{array}{c}O\\ \|\\ O\end{array}\right)$$

,



$$\mathrm{Au}\cdots\left(\begin{array}{c}H_2C\\ \|\\ CH_2\end{array}\right)$$

and



$$\mathrm{Ag}\cdots\left(\begin{array}{c}H_2C\\ \|\\ CH_2\end{array}\right)$$

,

yet conspicuous dissimilarity to $Ag(O_2)$ (see Fig. 4). Particularly noteworthy is the fact that $Ag(O_2)$ is colorless [4] and shows no absorptions above 220 nm, whereas $Au(O_2)$ [14], $(C_2H_4)Au$ and $(C_2H_4)Ag$ are, respectively, gree, green and purple (Figs. 2 and 4). On the basis of the frequencies of their $\nu(O{—}O)$ stretching modes alone, $Ag(O_2)$ (1080 cm^{-1}) and $Au(O_2)$

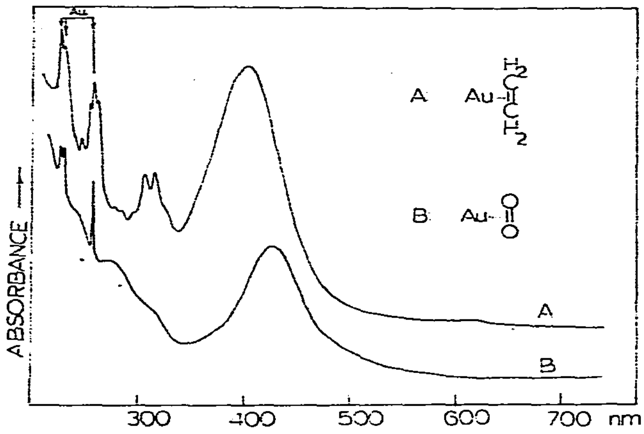


Fig. 4. The UV-visible spectra of (A) $(C_2H_4)Au$ and (B) $Au(O_2)$ in $^{12}C_2H_4/Ar \simeq 1:10$ and $^{16}O_2/Ar \simeq 1:10$ matrices at 8—10 K. Lines ascribed to trace amounts of Au atoms are indicated with arrows.

(1092 cm^{-1}) might initially be suspected of being $M^+(O_2^-)$ ion-pairs. * Although the absence of visible absorptions for $Ag(O_2)$ is consistent with the presence of superoxide and a formally (+1) silver oxidation state, such a bonding description is untenable for the green complex, $Au(O_2)$.

In view of the fact that the $\nu(O=O)$ stretching frequencies of transition metal dioxygen complexes are not a reliable indicator of the extent of the metal-dioxygen charge transfer [15], we would like to propose that the gold—dioxygen bonding interaction in $Au(O_2)$ is more closely akin to the Dewar description of metal—olefin bonding applicable to complexes such as $(C_2H_4)Au$ and $(C_2H_4)Ag$, rather than the extreme case of ion-pair bonding which appears to be an appropriate description for $Ag^+(O_2^-)$. Consistent with these bonding proposals are (i) the substantially lower first ionization potential of Ag (7.57 eV) compared to Au (9.22 eV) and (ii) the blue-shifted metal → ethylene π-charge transfer transition on passing from $(C_2H_4)Ag$ to $(C_2H_4)Au$.

Acknowledgements

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* $^{16}O_2/^{16}O^{18}O/^{18}O_2$ infrared matrix isolation experiments show that the dioxygen moiety is most probabley side-on bonding with respect to the metal in both $Ag(O_2)$ [4] and $Au(O_2)$ [14].

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