

Note

Raman spectroscopic investigations of dinuclear gold ylide complexes; further relationships of Au–Au bond lengths versus Au–Au stretching frequencies

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Received 12 August 1999; received in revised form 13 October 1999

Dedicated to Professor F.A. Cotton on the occasion of his 70th birthday.

Abstract

Raman spectroscopic data have been collected for the singly bonded Au(II) halogen complexes $\text{Au}_2(\text{MTP})_2\text{X}_2$ (MTP = $\text{CH}_2\text{P}(\text{S})\text{Ph}_2$; X = Cl, Br, I) with bands at 157, 125, and 105 cm^{-1} for Cl, Br, and I, respectively, being assigned to $\nu(\text{Au}-\text{Au})$. The corresponding Au–X vibrations have also been identified. The trend observed in the shift of $\nu(\text{Au}-\text{Au})$ with changes in halogen is comparable to the situation with the analogous $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$ series reported by Clark et al., for which the corresponding values are 162, 132, and 103 cm^{-1} . In both cases, these data show a trend toward decreasing Au–Au and Au–X stretching frequencies with increasing halide size. Interestingly, a plot of $r(\text{Au}-\text{Au})$ versus $\nu(\text{Au}-\text{Au})$ for the six oxidized complexes does not yield a single line, but instead two nearly parallel lines. The general relationship between metal–metal bond lengths and stretching vibrations for the six complexes are compared with other single-bonded dinuclear complexes in the light of various proposed empirical relationships. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Raman; Gold(II); Gold–gold vibration

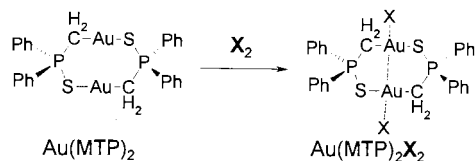
1. Introduction

There is a well-established tendency of gold to be attracted to and form bonds with itself, a subject of great interest in recent years [1]. Although not yet completely understood, it is manifest not only in a number of gold complexes containing actual metal–metal bonds, but also in many instances where unsupported, short gold–gold contacts are observed [2] in neutral complexes. Current literature is replete with examples of gold–gold separations ranging from 2.76 Å, for $[\text{Au}(i\text{-MNT})]_2^{3-}$, to about 3.5 Å [3]. The dinuclear Au(II) complexes [4] $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$ and $(\text{AuMTP})_2\text{X}_2$ (MTP = $\text{CH}_2(\text{S})\text{PPh}_2$; X = Cl, Br, I) have

even shorter Au(II)–Au(II) contacts, changing from about 3.0 Å in the bridged unoxidized Au(I) materials to around 2.6 Å following chemical oxidation (Scheme 1) [1,2d]. This dramatic decrease results from the formation of two Au–X bonds and a single Au–Au bond along a common axis and allows the opportunity to study stable d^9-d^9 systems. Initial work with these novel Au(II)–Au(II) systems focussed on the extent of the gold–gold interaction using such techniques as X-ray crystallography, which revealed that the bond lengths varied, increasing with increasing halide size. In order to further examine this change in gold–gold interaction with changing halide, Clark and co-workers used Raman spectroscopy [5,6] to obtain data on the metal–metal stretching vibrations in the dimethyl-ylide complexes. Their results allowed assignment of the Au–Au and Au–X stretching frequencies in that series.

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Scheme 1.

In the many other dinuclear complexes studied with Raman spectroscopy, there appears to be a relationship between the metal–metal distance and the corresponding empirical force constant. One formula, proposed by Woodruff and co-workers [7] for 4d and 5d metals, relates the exponent of the M–M stretching force constant to the M–M separation. For 5d metals in particular, this relationship has the form $r(5d) = 2.04 + 1.32 \exp(-F/2.17)$. Perreault et al. have recently pointed out [8] that this relationship may not be entirely valid for all 5d metals, particularly dinuclear gold complexes. They have proposed the equation $r(\text{Au}_2) = 0.290 \ln F(\text{Au}_2) + 2.68$ on the basis of data for various Au–Au species, the equation being derived from a simple Herschbach–Laurie relationship of a plot of Au–Au separations versus Au–Au stretching force constants. Of the complexes used in the derivation of this relationship, two were found to deviate fairly significantly from the plot, these being $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$ and $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{Cl}_2$. The authors proposed that the value of F may be ‘wrongly estimated’ using a diatomic model due to the ‘rigidity’ of the ylide ligand. We have noted that in the case of the oxidized complex there also may be some kinematic coupling of the bound halide atoms interacting directly along the axis of the Au–Au symmetric stretching motion. In an effort to examine further the relationship between Au–Au separations and stretching frequencies, while considering the possible influence of the halides and bridging ligands in these dinuclear gold ylidic complexes, we have obtained Raman spectroscopic data for the analogous $(\text{AuMTP})_2\text{X}_2$ series. Results are compared with those reported for $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$ and discussed in light of the various empirical bond distance-to-force constant relationships proposed for diatomic transition metal complexes.

2. Experimental

Samples were prepared at Texas A&M University using methods described elsewhere [4]. Raman data were collected at Los Alamos National Laboratory. Undispersed solid samples were used. Samples were loaded into a 5 mm NMR tube for room-temperature (r.t.) measurements, or secured to the copper block of a cryostat assembly with Dow-Corning 340 silicon heat

sink compound for low-temperature measurements. The cryostatic unit was routinely pumped several hours with an oil diffusion pump, then cooled overnight to an average temperature of 20 K using circulating liquid helium. Samples were irradiated with 600 or 620 nm laser lines generated by a Coherent CR599 tunable dye laser using rhodamine R6G as the lasing dye. The dye laser was pumped by a Spectra-Physics 2045E argon laser. In addition, the beams were attenuated to 20–30 mW at the source, which were further reduced to about half these values at the sample by virtue of the optics used to reflect and focus the beams. The back-scattered light from the samples was collimated and passed through a Spex double monochromator with 1800 line mm^{-1} Jobin–Yvon holographic gratings, driven by a Spex Compudrive CD2. Detection of the scattered radiation was by standard photon-counting techniques employing water-cooled RCA C31034 photomultipliers. Signals were processed via a Stanford Research Systems SR400 two-channel gated photon counter linked to a Macintosh SE computer. Data were stored on disks and processed at Texas A&M University using the IGOR plotting and analysis program by Wavemetrics on a Macintosh Iifx computer. In addition, all spectra were referenced to the 950 cm^{-1} peak of solid K_2SO_4 . The region of interest, $50\text{--}400 \text{ cm}^{-1}$, was determined from preliminary scans and by the results of Neira [5], as reported by Clark et al. [6]. Spectra were collected out to 600 cm^{-1} ; preliminary scans to 1100 cm^{-1} showed no major features beyond 600 cm^{-1} . The spectrum of $\text{Au}_2(\text{MTP})_2\text{Cl}_2$ was collected at r.t. using 600 nm radiation, while the data for the other two complexes were collected at 20 K with 620 nm radiation.

3. Results and discussion

X-ray crystallographic data on $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$ and $[\text{AuCH}_2(\text{S})\text{PPh}_2]_2\text{X}_2$ indicate that they exist as discrete species in the solid state. Furthermore, the gold-metallo-ring framework is largely unaffected upon oxidation. While no clear assignments could be made for bands in the Raman spectrum of the unoxidized $(\text{AuMTP})_2$ complex, bands are observed at 54, 57 and 65 cm^{-1} , values similar to those reported for the metalla-ring vibrations, 64 cm^{-1} , of $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$. The assignments made for the $\nu(\text{Au–Au})$ and $\nu(\text{Au–X})$ bands in the gold dimethylene ylide complex can be compared directly with those of the MTP complex, assuming that the linear X–Au–Au–X moiety is vibrationally isolated from the ring system. These Au–Au and Au–X stretching signals are expected to be well-enough separated from the other metalla-ring vibrations to permit facile identification. On this basis, the assignments for $\nu(\text{Au–Au})$ and $\nu(\text{Au–X})$ given in Table 1 have been made. The corresponding values

Table 1
Bond lengths (Å), $\nu(\text{Au–Au})$, and $\nu(\text{Au–X})$ (cm^{-1}) for $(\text{AuMTP})_2\text{X}_2$

X	$r(\text{Au–Au})$	$\nu(\text{Au–Au})$	$\nu(\text{Au–X})$
Cl	2.553	157	298
Br	2.593	125	222
I	2.608	105	191

Table 2
Bond lengths (Å), $\nu(\text{Au–Au})$, and $\nu(\text{Au–X})$ (cm^{-1}) for $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$

X	$r(\text{Au–Au})$	$\nu(\text{Au–Au})$	$\nu(\text{Au–X})$
Cl	2.597	162	293
Br	2.617	132	220
I	2.650	103	165
NoX	3.01	54–65(b)	–
NoX	2.977	64	–

Table 3
Comparison of $\nu(\text{M–M})$ (cm^{-1}) for $(\text{AuMTP})_2\text{X}_2$, $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$, Hg_2X_2 , and $\text{K}_4[\text{Pt}_2(\text{pop})_4\text{X}_2]$

Complex	X	$\nu(\text{M–M})$
$(\text{AuMTP})_2\text{X}_2$	Cl	157
	Br	125
	I	105
$[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$ ^a	Cl	162
	Br	132
	I	103
Hg_2X_2 ^b	Cl	166
	Br	132
$\text{K}_4[\text{Pt}_2(\text{pop})_4\text{X}_2]$ ^c	Cl	158
	Br	133
	I	105

^a Ref. [5,6].

^b Ref. [9].

^c Ref. [10].

Table 4
Comparison of $\nu(\text{Au–X})$ (cm^{-1}) for various gold–halogen complexes

Complex	X = Cl	X = Br	X = I
$(\text{AuMTP})_2\text{X}_2$	298	222	191
$[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$	293	220	165 ^a
$[\text{AuX}_2]^-$	329	209	158 ^b
$[\text{Ph}_3\text{PAuX}]$	329	229	187 ^c

^a Ref. [5,6].

^b Ref. [12].

^c Ref. [13].

reported for $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$ are presented in Table 2. Upon oxidation of the Au(I) complexes, the corresponding stretching frequencies are expected to increase as the Au–Au bond order increases from zero to one, and this is what is observed in both the dimethylene and thiomethylene systems. This trend has been ob-

served in other oxidized dinuclear complexes, most notably Hg_2X_2 [9] and $\text{K}_4[\text{Pt}_2(\text{pop})_4\text{X}_2]$ ($\text{pop} = \text{P}_2\text{O}_5\text{H}_2^{2-}$) [10]. These values are compared in Table 3. Additionally, the lowering of the Au–X stretching frequency with increasing halide mass is expected and has been noted for several other unrelated gold–halide complexes in Table 4.

The assumption that the ring vibrations do not interact with the linear X–Au–Au–X motions is intuitively too simplistic, although not necessarily completely invalid. The replacement of a methylene group in the ylide ligand with a sulfur atom in the MTP ligand shifts the frequencies in the MTP complexes with X = Cl or Br to slightly lower values relative to the corresponding ylide complexes, presumably due to coupling of the ring bending motions to the Au–Au and Au–X stretching motions. When X = I, the mass of the iodine atom relative to gold appears to overwhelm any difference in ring contributions between the ylide and MTP species, giving them roughly the same Au–Au stretching frequency. The shift of $\nu(\text{Au–Au})$ to lower values with increasing halide mass is expected on the basis of increasing bond lengths and concurs with the results of Neira [5,6].

A question we wished to address concerns the relationship between Au–Au bond lengths and corresponding vibrational frequencies in these complexes. While there are not enough data to calculate true values for $F(\text{Au–Au})$ in these systems, the relationship between $r(\text{Au–Au})$ and $\nu(\text{Au–Au})$ may be seen in the plot shown in Fig. 1. Interestingly, the data for these two bridging ligand systems do not form a single line, but two nearly parallel lines, one for each series. Even if the force constants are approximated from the frequencies by using the simple relationship $F(\text{Au}_2) = \mu[2\pi c\nu(\text{Au}_2)]^2$, the data could not be merged into a single line described by a simple mathematical relationship. A comparison of these estimated $F_{\text{Au–Au}}$ values versus $r_{\text{Au–Au}}$ is presented in Table 5. When the simple approximation is used, the force constants deviate tremendously from those obtained from the relationship developed by Woodruff and co-workers for 5d metals [7] or from the relationship of $\ln F$ versus $r(\text{Au}\cdots\text{Au})$ proposed by Perreault et al. for dinuclear Au species [8]. If the force constants are estimated using a simple X–Au–Au–X linear approximation, neglecting the off-diagonal terms [11], the values come closer to those calculated from the Perreault equation, but still do not match either set very well.

One reason that the calculated force constants for the $\text{Au}(\text{MTP})_2\text{X}_2$ complexes vary so much from the empirical relationships may have to do with the direct gold–halide interactions along the axis of the symmetric stretch. With the exception of the $\text{Au}_2(\text{ylide})_2\text{Cl}_2$ complex and Au_2 in various states, none of the species used in the derivation of the relationship of Perreault et al.

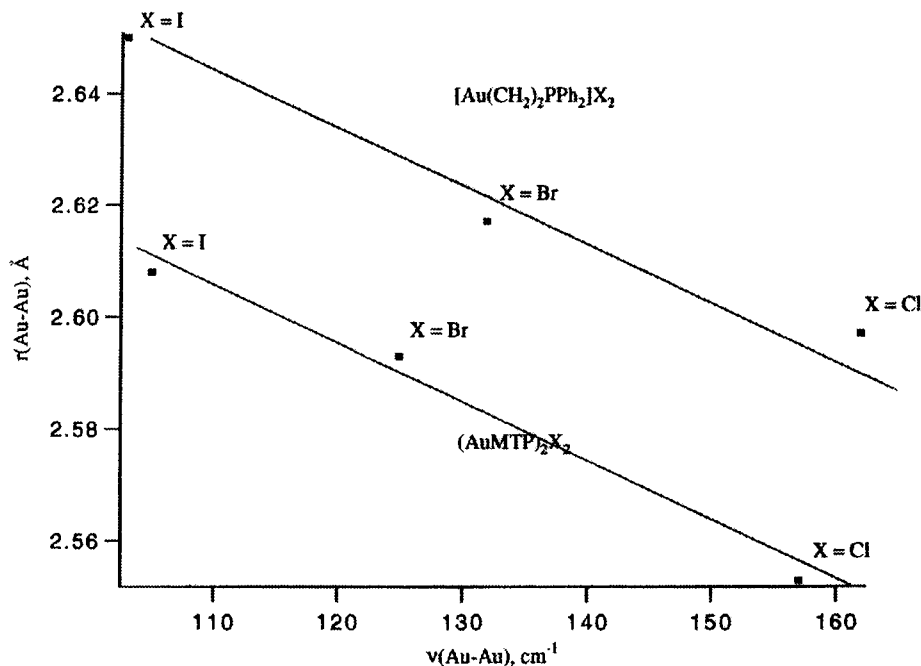


Fig. 1. Plot of $r(\text{Au}-\text{Au})$ vs. $\nu(\text{Au}-\text{Au})$ for $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$ and $(\text{AuMTP})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

Table 5
 $F(\text{Au}-\text{Au})$ (mdyne \AA^{-1}) values for $(\text{AuMTP})_2\text{X}_2$ and $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$ using: (a) $F(\text{Au}_2) = \mu(2\pi c\nu(\text{Au}_2))^2$ (ν in cm^{-1}); (b) calculation from a linear $\text{X}-\text{Au}-\text{Au}-\text{X}$ model ignoring off-diagonal terms; (c) $r(5d) = 2.04 + 1.32 \exp(-F/2.17)$; and (d) $r(\text{Au}_2) = 0.290 \ln F(\text{Au}_2) + 2.68$ (r in \AA)

Complex	X	$F(\text{Au}-\text{Au})$, (mdyne \AA^{-1})		$r(5d)$ (\AA)		$r(\text{Au}_2)$ (\AA)	
		(a)	(b)	(c)	(d)		
$(\text{AuMTP})_2\text{X}_2$	Cl	1.430	1.824	2.051	1.549		
	Br	0.906	1.685	1.888	1.349		
	I	0.639	1.566	1.830	1.282		
$[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$	Cl	1.520	1.914	1.872	1.331		
	Br	1.010	1.736	1.796	1.243		
	I	0.615	1.558	1.675	1.109		

involves a true metal–metal bond. There may be an inherent problem in trying to relate force constants where a true metal–metal bond exists to those calculated from systems in which the apparent Au–Au frequencies are the result of relativistic and correlation interactions [1a,2a]. In addition, the halide masses appear to have a profound effect on the ‘pure’ Au–Au stretch, as the Au–X stretches couple directly along this common axis.

Secondly, the results of this study seem to indicate that a linear X–Au–Au–X model is too simplistic to be used in ring systems with these bridging ligands. The only structural difference between these two complexes is a sulfur atom versus a methylene group. The fact that two different linear relationships hold for slightly different bridged complexes implies that the ring has an inherent effect on the systems. If the distance between gold atoms in ring systems is defined solely by ligand

bite angles, then a modified equation should be proposed which accounts for the influence of a particular ring on the Au–Au separation. Such an equation must consider factors such as ring size and mass, steric hindrance, and whether or not atoms of comparable mass interact directly along the metal–metal vector. If $r(\text{Au}-\text{Au})$ versus $\ln F(\text{Au}-\text{Au})$ for the ylide and MTP complexes are plotted along with the data used by Perreault et al., the resulting line (Fig. 2) has the equation:

$$r(\text{Au}_2) = -0.276 \ln F(\text{Au}_2) + 2.71 \quad (1)$$

which is not very different from the original equation, but better represents the influence of metal–metal bonded ring systems to the overall relationship. Raman data on analogous gold dithiophosphate or dithiolate systems may further support this position, possibly

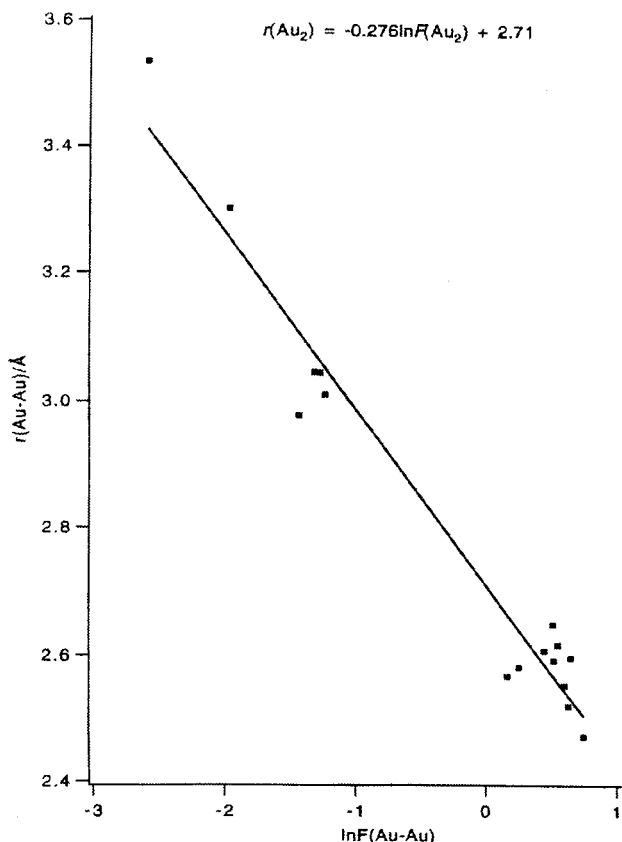


Fig. 2. Plot of $r(\text{Au-Au})$ vs. $F(\text{Au-Au})$ for various dinuclear gold species.

resulting in additional lines parallel to the two observed in this study, as well as further modifying the generalized $r(\text{Au-Au})/F(\text{Au-Au})$ relationship to give better approximations when rings are involved.

4. Conclusions

The results of the Raman spectroscopic measurements of $(\text{AuMTP})_2\text{X}_2$ indicate that the Au–Au and Au–X stretching frequencies in this system decrease with increasing bond length, which is in turn influenced by the mass of the interacting halide. This trend concurs with that of other singly bonded oxidized complexes, most notably $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]\text{X}_2$ and $\text{K}_4[\text{Pt}_2(\text{pop})_4\text{X}_2]$. In addition, the relationship between $r(\text{Au-Au})$ and $\nu(\text{Au-Au})$ does not appear to be solely dependent on gold–gold separation, but also upon the type of bridging ligand involved.

Acknowledgements

We wish to thank Dr W.H. Woodruff and the Los Alamos National Laboratory for providing the Raman

equipment and facilities used for this study and some sample measurements. We would also like to thank the National Science Foundation (NSF Grant CHE 8708625), the Robert A. Welch Foundation and the Texas Advanced Research Program for funding this research.

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