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^{197}Au-Mössbauer Spectroscopic Studies of Monomeric and Trimeric Gold(I) Azolates

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Synopsis. The identical chemical state of three gold atoms in trimeric gold(I) azolates and the Au(I)–Au(III) mixed-valence state in their iodine adducts, $Au_3(az)_3I_2$, were confirmed by means of ^{197}Au-Mössbauer spectroscopy.

^{197}Au-Mössbauer spectroscopy is one of the most useful techniques in the structural diagnosis of gold(I) compounds because the Mössbauer parameters are very sensitive to the number and nature of ligands coordinated with the gold atom.

Recently, stable gold(I) derivatives of several azoles have been prepared by Minghetii *et al.*[1] A nine-membered-ring structure containing three gold atoms in a molecule has been suggested in several cases. Some of these trimeric compounds react with iodine to give mixed-valence compounds.

It is our purpose to confirm the trimeric structure and mixed-valence state of gold in several iodine adducts, $Au_3(az)_3I_2$. The present paper will describe the results obtained by ^{197}Au-Mössbauer spectroscopy for monomeric and trimeric gold(I) derivatives of several azoles and their iodine adducts.

Experimental

Materials. The $Au_3(az)_3$ (az=pyrazolato, (pz); 3,5-dimethylpyrazolato, (3,5-Me_2-pz); 3,5-dimethyl-4-iodopyrazolato, (3,5-Me_2-4-I-pz); or benzo-1,2,3-triazolato, (btaz)), Au_3(3,5-Me_2-pz)$_3I_2$, Ph_3PAu(btaz), and Ph_3PAu(3,5-Me_2-pz) were prepared by following the method described in the literature.[1] The $Au_3(pz)_3I_2$ was prepared by a method similar to that described in Ref. 1. The purity of the samples was checked by elemental analysis.

Measurements. ^{197}Au-Mössbauer spectroscopic measurements were carried out with a source and an absorber, both cooled to 18 K by using a constant acceleration-type spectrometer accompanied with a pure-Ge diode detector. Details of the ^{197}Au-Mössbauer spectroscopy were described in our previous study.[2] All the values of isomer shifts are referred to metallic gold at 18 K. The precision of the Mössbauer parameters obtained is within ±0.04 mm/s.

Results and Discussion

Mössbauer parameters, such as the isomer shift (*IS*), the quadrupole splitting (*QS*), and the half-width (Γ_{exp}), are summarized in Table 1, while some typical spectra are shown in Fig. 1. The values of *IS* and *QS* for Ph_3PAu(btaz) are smaller than those of Ph_3Au(3,5-Me_2-pz). This may be ascribed to the reduction of the σ-donating ability of nitrogen by the fused benzene ring. The Mössbauer parameters of monomeric gold(I) azolates are similar to those of the same type of compounds, $[Ph_3PAuL]^+$ (L=C_5H_5N, $C_5H_{10}NH$, or $[N_3]^-$), reported previously.[3,4]

TABLE 1. MÖSSBAUER PARAMETERS OF GOLD(I) AZOLATES AND THEIR IODINE ADDUCTS

Compound		*IS* mm s^{-1}	*QS* mm s^{-1}	Γ_{exp} mm s^{-1}
Ph_3PAu(btaz)		4.38	8.32	2.04
Ph_3PAu(3,5-Me_2-pz)		4.78	9.00	1.95
$Au_3(btaz)_3$		3.44	6.98	2.35
$Au_3(pz)_3$		3.41	7.35	2.11
Au_3(3,5-Me_2-pz)$_3$		3.28	7.39	2.37
Au_3(3,5-Me_2-4-I-pz)$_3$		3.41	7.42	2.70
$Au_3(pz)_3I_2$	Au(I)	3.40	7.43	2.18
	Au(III)	3.31	3.67	2.06
Au_3(3,5-Me_2-pz)$_3I_2$	Au(I)	3.57	7.82	2.23
	Au(III)	3.40	3.92	2.14

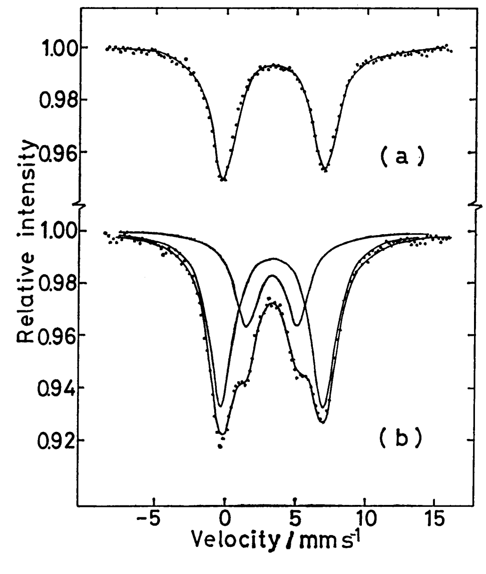

Fig. 1. Mössbauer spectra of (a) $Au_3(pz)_3$ and (b) $Au_3(pz)_3I_2$.
The full lines are least-squares fits of Lorentzians. The areal intensity ratio, $R=A_+/A_-$ was 0.96 for top spectrum. The lines of each pair for bottom spectrum were constrained to have equal intensities and widths.

In trimeric gold(I) azolates, the Mössbauer spectra consist of a single doublet, indicating that the three gold atoms in a molecule have an identical chemical state. This means that these compounds have a nine-membered-ring structure. Therefore, in trimeric compounds, the azole acts as an exobidentate *N,N'*-ligand,

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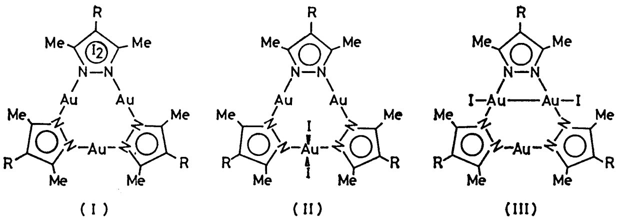

Fig. 2. Possible structures for iodine adducts (from Ref. 1).

forming a cyclic structure. Since the σ-donating ability of the azole ligand is smaller than that of triphenylphosphine, both the *IS* and *QS* values can be expected to decrease for the trimeric compound. A similar trend of the decrease in *IS* and *QS* values is observed on going from $[Ph_3PAuL]^+$ to $[AuL_2]^+$ ($L=C_5H_5N$, $C_5H_{10}NH$, or $[N_3]^-$).[3,5]

Trimeric gold(I) azolates are stable to air, moisture, and heat and are sparingly soluble in most organic solvents. Those compounds are very stable toward alkalis and acids, but the reaction of trimeric gold(I) azolates with iodine is carried out readily in chloroform and gives only 1:1 adducts, even in the presence of excess iodine. Three kinds of possible structures for these adducts were proposed by Minghetti *et al.* (*cf.* Fig. 2). Based on the results of the visible, IR, and ^{1}H-NMR spectra, they suggested for the adducts the type-II structure. The ^{197}Au-Mössbauer spectra of $Au_3(pz)_3I_2$ and $Au_3(3,5\text{-}Me_2\text{-}pz)_3I_2$ in the present studies show the presence of at least two different sites or oxidation states of gold. A typical spectrum of $Au_3(pz)_3I_2$ is shown in Fig. 2b. The estimated Mössbauer parameters for the adducts are listed in Table 1. One of the sets of parameters is almost the same as that of the original materials. From the Mössbauer parameters, the set is assigned to the Au(I) site which is not attached by iodine. The other set of Mössbauer parameters is very different from the original materials.

In ^{197}Au-Mössbauer spectroscopy, a linear relationship between the observed *IS* and *QS* values has been established for many gold(I) and gold(III) compounds.[6] The average of the literature values is given by:

$$QS = 1.74IS - 2.27\ \text{mm/s for Au(III)}, \qquad (1)$$

and:

$$QS = 1.06IS + 3.80\ \text{mm/s for Au(I)}, \qquad (2)$$

where the *IS* data are given relative to Au foil.

By using the *IS* data of the new peak components found in $Au_3(pz)_3I_2$ and $Au_3(3,5\text{-}Me_2\text{-}pz)_3I_2$ in Eq. 1, we can estimate the expected values of *QS* as 3.49 and 3.65 mm/s respectively for the adducts. A comparison of these values with the observed values in Table 1 suggests that the Mössbauer parameters of the gold atoms in the other site in the adducts are assigned to gold(III). Furthermore, the area intensity ratio of the absorption line of Au(I) and Au(III) sites is about 2:1. Thus, it may be concluded that the adducts with iodine are Au(I)–Au(III) mixed-valence compounds and have the type-II structure, as has been suggested by Minghetti *et al.*

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