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^{197}Au Mössbauer Spectra of Binuclear Gold(I) and Gold(II) Complexes Containing Bridging Cyclometalated Arylphosphine or Arylarsine Ligands

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The gold-197 Mössbauer parameters have been determined at 20 K for three binuclear gold(I) complexes $[Au_2(C_6H_4E)_2]$ ($E=PEt_2$, PPh_2, $AsPPh_2$) and for three complexes formed from them by halogenation, viz. $[Au_2(C_6H_4E)_2X_2]$ ($E=PEt_2$, $X=I$; $E=PPh_2$, $X=I$; $E=PPh_2$, $X=Br$). The results show that the gold atoms in the latter compounds are equivalent and thus confirm the gold(II)-gold(II) formulation.

Gold-197 Mössbauer spectroscopy has been used to elucidate the structure and bonding in a range of compounds of this element.$^{1,2)}$ For example, ^{197}Au Mössbauer spectra showed that the complexes $(L)_nAu_2Cl_4$ (L=olefin or acetylene; n=1,2), which were considered for many years to be derivatives of gold(II), in fact contain equal amounts of gold(I) and gold(III).

The first gold(II) complex characterized by ESCA and ^{197}Au Mössbauer spectroscopy was $[\{Et_2P(CH_2)_2AuBr\}_2]$.$^{3)}$ To date, only nine sets of ^{197}Au Mössbauer parameters have been reported for binuclear gold(II) complexes, including $[Me_2C(PPh_2AuCl_2)_2]$,$^{4)}$ $[Me_2C(PPh_2AuClBr)_2]$,$^{4)}$ $[MeN(PPh_2AuCl_2)_2]$$^{5)}$ and $[R(X)Au(Ph_2PNHPPh_2)Au(X)R]$ (X=Cl, Br, I; $R=C_6F_5$, C_6Cl_5).$^{6)}$ Recently, Bennett et al. prepared binuclear cyclometalated complexes of gold(I) (**1** - **3**)$^{7)}$ and gold(II) (**4** - **6**)$^{8)}$ and determined the structure of **1** - **3** and **5** by X-ray crystallography.

In this letter, we report a Mössbauer spectroscopic study of these

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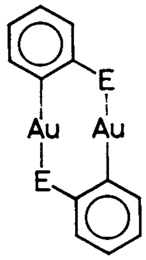
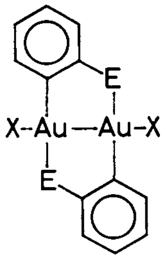


1, E=PEt$_2$
2, E=PPh$_2$
3, E=AsPh$_2$



4, E=PEt$_2$, X=I
5, E=PPh$_2$, X=I
6, E=PPh$_2$, X=Br

complexes. Gold-197 Mössbauer spectra were obtained by an Austin Science S-600 Mössbauer spectrometer with both source and absorber kept at 20 K in a cryostat incorporating a closed cycle refrigerator,[9] using ^{197}Pt in platinum metal as a source with a pure Ge solid state detector. The source was made by neutron-irradiation of a 100 mg disk of metallic Pt enriched to 97.5% in ^{196}Pt. The absorber thickness was about 200 mg Au cm^{-2}. The data were analysed by the usual least-squares method. The isomer shift is given relative to ^{197}Pt in Pt metal.

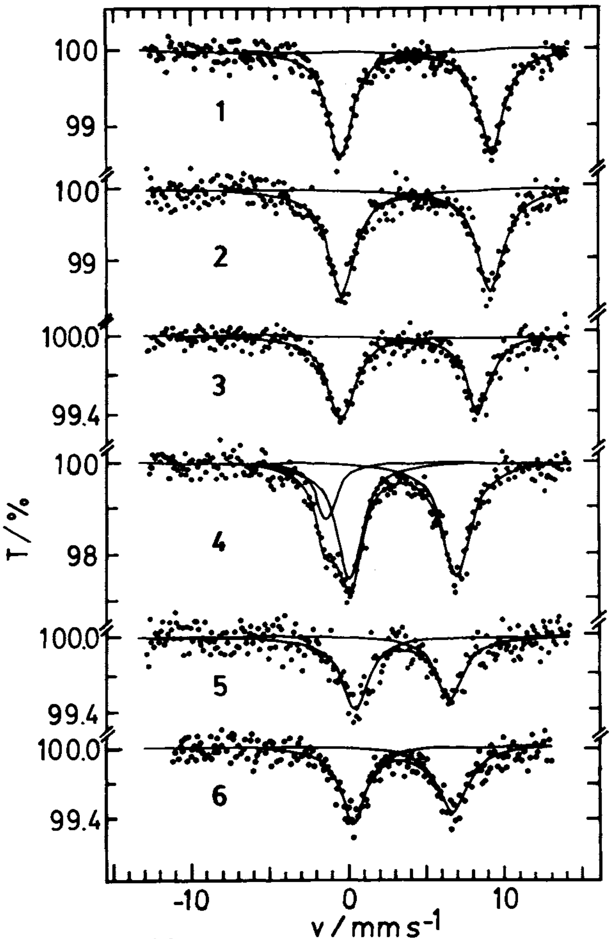


Fig. 1. ^{197}Au Mössbauer specta at 20 K of gold(I) and gold(II) complexes.

The results are shown in Fig. 1 and Table 1. The Mössbauer spectra consist of a well resolved quadrupole doublet. The appearance of an additional singlet (B) in the Mössbauer spectrum of **4** indicates the presence of small amounts of metallic gold formed by decomposition. The main doublet (A) has parameters similar to those for the structurally characterized binuclear gold(II) complex **5**. Thus the Mössbauer results clearly show that **4** and **6**, like **5**, are isovalent gold(II)-gold(II) (d^9-d^9) complexes, not heterovalent gold(I)-gold(III) (d^{10}-d^8) complexes.

The isomer shifts (IS) and quadrupole splittings (QS) for [Au$_2$(C$_6$H$_4$-E)$_2$] are typical of Au(I) complexes and decrease in the order E=PEt$_2$ > PPh$_2$ > AsPh$_2$. This is the order of decreasing electron-donation by ligand, E,

Table 1. ^{197}Au Mössbauer Parameters at 20 K for Gold(I) Complexes (**1** - **3**) and Gold(II) Complexes (**4** - **6**)

	compound		IS/mm s^{-1} a) (±0.10)	QS/mm s^{-1} (±0.10)	Γ/mm s^{-1} b) (±0.2)
1	[$Au_2(C_6H_4PEt_2)_2$]		4.67	10.12	2.0, 2.0
2	[$Au_2(C_6H_4PPh_2)_2$]		4.53	9.58	2.0, 2.1
3	[$Au_2(C_6H_4AsPh_2)_2$]		4.08	8.80	2.1, 2.0
4	[$Au_2(C_6H_4PEt_2)_2I_2$]	(A)	3.60	6.96	2.2, 2.2
		(B)	-1.23	0	1.7
5	[$Au_2(C_6H_4PPh_2)_2I_2$]		3.46	6.54	2.3, 1.9
6	[$Au_2(C_6H_4PPh_2)_2Br_2$]		3.46	6.44	2.4, 2.1

a) The IS value of 2.85 mm s^{-1} obtained for Ph_3PAuCl at 20 K agreed with 2.83 mm s^{-1} at 4.2 K reported by Schmidbaur et al.[3]

b) Γ means experimental line width (FWHM).

into the sp hybrid orbitals of the C-Au-P unit. It correlates with decreasing IS and QS values in the order [$Au(PEt_3)_2$]$^+$ > [$Au(PPh_3)_2$]$^+$ > [$Au(AsPPh_3)_2$]$^+$.[10] The complexes **1** - **3** contain the eight membered $Au_2C_4P_2$ or $Au_2C_4As_2$ heterocycle in a boat conformation, the Au(I)-Au(I) distances being 2.86, 2.86 and 2.94 Å for **1**, **2**,and **3**, respectively, close to that in metallic gold (2.88 Å). The IS and QS values for **1** and **2** are less than those of Ph_3PAuPh (IS=5.01 mm s^{-1}, QS=10.24 mm s^{-1}),[11] perhaps due to the neighboring metal atom, which effectively increases the coordination number of the gold(I) atom.

It is interesting to note that the complexes **1** and **2** have larger isomer shifts than other binuclear gold(I) complexes containing either C-Au-P coordination (IS=3.99 - 4.43 mm s^{-1})[6,12] or even C-Au-C coordination (IS= 3.76 mm s^{-1}) in [$\{Et_2P(CH_2)_2Au\}_2$].[3] The metal-metal separations in **1** and **2** are less than in the ylide complex (3.02 Å), [13] suggesting that there is a larger contribution to the 6s population from the gold-gold interaction in **1** and **2**, thus resulting in larger IS values.

Both IS values (3.46 - 3.60 mm s^{-1}) and QS values (6.44 - 6.96 mm s^{-1}) for the gold(II)-gold(II) complexes **4** - **6** are much less than those for the corresponding gold(I)-gold(I) complexes **1** and **2**. A similar trend is evident in other systems. The observed reductions in the values of IS (1.07 mm s^{-1}) and QS (3.04 - 3.16 mm s^{-1}) in our complexes are comparable with those in [$\{Et_2P(CH_2)_2AuBr\}_2$] and [$MeN(PPh_2AuCl_2)_2$] (ΔIS=1.09 - 1.11 mm s^{-1}, ΔQS=2.89 - 3.39 mm s^{-1},[3,5]) and [R(X)Au($Ph_2PNHPPh_2$)Au(X)R] (X=Cl, Br, I; R=C_6F_5) (ΔIS=0.90 - 1.09 mm s^{-1}, ΔQS=3.32 - 3.44 mm s^{-1}).[6]

Compound **5** has four coordinated square-planar gold(II), PAu(Au)CI, the

Au(II)-Au(II) distances being 2.59 and 2.60 Å for two independent molecules; these are significantly shorter than the corresponding separation in the Au(I)-Au(I) precursor **2**. The dsp^2 hybridization for Au(II) (d^9) would cause s electron densities at the gold nucleus to be smaller than for sp-hybridized Au(I) (d^{10}). This would result in smaller IS values for the Au(II) complexes.

Finally it should be noted that our gold(II) complexes **4** - **6** with PAu(Au)CX coordination (X=I,Br) have larger IS values than do the gold(II) ylide complex $[\{Et_2P(CH_2)_2AuBr\}_2]$ with CAu(Au)CBr coordination (IS=2.67 mm s^{-1}, QS=6.71 mm s^{-1}) and gold(II) bis(biphenylphosphino)amine complexes $[R(X)Au(Ph_2PNHPPh_2)Au(X)R]$ (X=Cl, Br, I; $R=C_6F_5$, C_6Cl_5) with PAu(Au)CX coordination (X=Cl, Br, I; IS=2.90 - 3.09 mm s^{-1}, QS=6.20 - 6.59 mm s^{-1}).

In summary, the results provide clear evidence for the formulation of **4** - **6** as isovalent Au(II) complexes. The IS and QS values for the Au(II) atoms in the gold(II)-gold(II) complexes containing cyclometalated tertiary phosphine ligands were found to be considerably smaller than those for the corresponding gold(I)-gold(I) binuclear complexes, **1** - **3**. In addition, the IS and QS values obtained are the largest observed for the binuclear gold(I) compounds with C(Au)P coordination and for gold(II) compounds with PAu(Au)CX (X=Cl, Br, I)$^{6)}$, CAu(Au)CBr$^{3)}$, and PAu(Au)ClX (X=Cl,Br)$^{4,5)}$ coordination.

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References

1) H.D. Bartunik and G. Kaindl, "Mössbauer Isomer Shifts," ed by G.K. Shenoy and F.E. Wagner, North-Holland, Amsterdam (1978), p.515.
2) R.V. Parish, "Mössbauer Spectroscopy Applied to Inorganic Chemistry," ed by G.J. Long, Plenum, New York (1984), p.577.
3) H. Schmidbaur, J.R. Mandl, F.E. Wagner, D.F. Van de Vondel, and G.P. Van der Kelen, *J. Chem. Soc., Chem. Commun.*, **1976**, 170.
4) H. Schmidbaur, A. Wohlleben, F.E. Wagner, D.F. Van de Vondel, and G.P. Van der Kelen, *Chem. Ber.*, **110**, 2758 (1977).
5) H. Schmidbaur, F.E. Wagner, and A. Wohlleben-Hammer, *Chem. Ber.*, **112**, 496 (1979).
6) L.S. Moore, R.V. Parish, R. Usón, A. Laguna, M. Laguna, and M.N. Fraile, *J. Chem. Soc., Dalton Trans.*, **1988**, 23.
7) M.A. Bennett, S.K. Bhargava, K.D. Griffiths, G.B. Robertson, W.A. Wickramasinghe, and A.C. Willis, *Angew. Chem., Int. Ed. Engl.*, **26**, 258 (1987).
8) M.A. Bennett, S.K. Bhargava, K.D. Griffiths, and G.B. Robertson, *Angew. Chem., Int. Ed. Engl.*, **26**, 260 (1987).
9) T. Takano, Y. Ito, and M. Takeda, *Radioisotopes*, **29**, 29 (1980).
10) P.G. Jones, A.G. Maddock, M.J. Mays, M.M. Muir, and A.F. Williams, *J. Chem. Soc., Dalton Trans.*, **1977**, 1434.
11) M. Katada, Y. Uchida, H. Sano, H.H. Wei, H. Sakai, and Y. Maeda, *Radiochem. Radioanal. Lett.*, **54**, 55 (1982). The IS reported relative to metallic gold was converted to the value relative to Pt-197/Pt source by subtracting 1.20 mm/s.
12) J.A.J. Jarvis, A. Johnson, and R.J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, **1973**, 373.
13) H. Schmidbaur, J.E. Mandl, W. Richter, V. Bejenke, A. Frank, and G. Huttner, *Chem. Ber.*, **110**, 2236 (1977).

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