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A gold-197 Mössbauer investigation of C-, S-, and N-derivatives of R_3PAu^I

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Abstract

Mössbauer parameters for various $(R_3P)AuQ$ compounds (R is Ph or cyclohexyl; $[Q]^-$ is a substituted acetylide, a thiolate, or a C-, S- or N-derivative of a heterocycle) show that gold is two-coordinated in the solid state. Though sensitive to the type of carbon ligand, the parameters do not allow distinction between P–Au–C, P–Au–S, and P–Au–N coordination.

Introduction

In spite of the disadvantages of ^{197}Au Mössbauer spectroscopy, such as the short half-life of the ^{197}Pt isotope and the low recoil-free fraction, this technique is increasingly used in studies of the nature of bonding and of the structures of gold compounds. The available results have been summarized in reviews [1] and these should be supplemented by some more recent papers [2,3] to provide a picture of the rôle of Mössbauer spectroscopy in the chemistry of gold.

Since we have obtained and characterized several types of gold(I) compounds [4–6] containing a phosphine along with another ligand that can exist in tautomeric forms, it seemed of interest to record the Mössbauer spectra of some of them together with those of suitable reference compounds. An additional aim of such an investigation is to provide general information on the interaction between R_3PAu^I and heterocycles, especially because (tertiary phosphine)gold(I) derivatives are used in pharmacy not only against rheumatoid arthritis but also against certain forms of cancer; for the latter both triphenylphosphine [7] and bis(1,2-arylphosphino)ethane [8] derivatives are used.

Previously [3a] ^{197}Au spectroscopy was shown to be helpful in the assignment of the coordination environment around the gold atom in the solid state, even in the absence of crystals suitable for X-ray studies. We now report additional uses of the technique and point out some limitations when C-, S- or N-tautomers are possible.

Results and discussion

In some of the compounds investigated two coordination around gold is either likely (**1** and **14**) or has been confirmed by an X-ray crystal structure determination (compound **9** [5]), and so they can be used as references for the S–Au–P, C–Au–P or N–Au–P arrangement respectively. In the remaining complexes, two-coordination is not unlikely in terms of the spectral data used to identify them when they were reported, but, in the absence of X-ray crystal structures, the NMR or infrared spectral data obtained do not prove that the same compounds are also two-coordinate in the solid state. Such proof would be a welcome addition to the available knowledge: indeed, in some cases the isolated Q–Au–PR$_3$ molecule contains solvent (water in **3** or **6**, benzene in **9**), in other cases the QH ligand can exist in several tautomeric forms each of which could be metallated, and in all cases the [Q]$^-$ ligand contains additional electron pairs available for donation to the metal. For all these reasons, as well as because of the possibility of Au ··· Au interactions, in the solid state the coordination number can become higher than two as a result of inter- or intra-molecular bonding. All these possibilities can now be excluded

Table 1

^{197}Au Mössbauer parameters at 4.2 K

Compound [a]	IS [b,c]	QS [b]	−QS [b,d]	LW [b]	Ref.
1st family: P – Au – S					
LAuS(*m*-tolyl) (**1**)	3.04(1)	7.82(1)	7.98	1.92(1)	[6]
L′AuS(S)PPh$_2$ (**2**)	3.08(1)	8.10(3)	7.98	2.06(3)	[6]
6-(L′AuS)purine·H$_2$O (**3**)	3.09(1)	8.18(1)	7.98	1.97(2)	[6]
2-(LAuS)-5-CF$_3$-pyridone·0.5H$_2$O (**4**)	3.29(1)	8.27(1)	7.98	1.95(1)	[6]
1-Me-2(L′AuS)imidazole (**5**)	3.48(1)	8.38(1)	7.98	1.93(1)	[6]
2-(L′AuS)imidazole (**6**)	3.55(1)	8.43(1)	7.98	1.91(1)	[6]
2nd family: P – Au – N					
1-(LAu)-3-Et$_2$-pyrimidin-2,4,6-trione (**7**)	2.72(1)	8.22(2)	8.40	2.09(3)	[5]
N-(L′Au)saccharine (**8**)	3.17(1)	8.36(1)	8.40	1.92(2)	[6]
1,3-(LAu)$_2$-5-Et$_2$-pyrimidin-2,4,6-trione (**9**)	3.21(1)	8.53(9)	8.40	1.91(5)	[5]
N-(L′Au)-phthalimide (**10**)	3.23(1)	8.58(1)	8.40	1.95(3)	[6]
N′-(LAu)imidazolium picrate (**11**)	3.28(1)	8.55(2)	8.40	1.97(3)	[6]
3rd family: P – Au – C					
1,3-Me$_2$-5-(LAu)$_2$-pyrimidin-2,4,6-trione (**12**)	3.28(2)	8.49(2)	8.56	1.92(3)	[5]
1,3,5,5′-(LAu)$_4$-pyrimidin-2,4,6-trione (**13**)	3.41(1)	8.68(1)	8.56 [e]	2.04(2)	[5]
LAuC≡CPh (**14**)	4.12(1)	10.21(1)	10.14	1.93(2)	[6]
LAuC≡C(1-hydroxy-cyclohexyl) (**15**)	4.14(1)	10.30(1)	10.14	1.97(2)	[6]

[a] L denotes triphenylphosphine, L′ tri-cyclohexylphosphine. [b] In mm s^{-1}. [c] Reference to Pt/Au source. [d] Values calculated according to the point charge model. [e] Two QS values are calculated: 8.56 for the C–Au–P and 8.40 for N–Au–P sites, respectively.

because the compounds listed in Table 1 have Mössbauer parameters in the range typical of two coordination, i.e. IS 2.7–4.1 and QS 7.8–10.3 mm sec^{-1}.

For the compounds **1–6** infrared and NMR data suggest a P–Au–S arrangement, in agreement with the results of an X-ray crystal structure determination carried out [6] on a compound similar to **5**, namely 1-Me-2-(Cy_3PAu)imidazole · 2benzimidazole: here one benzimidazole is hydrogen bonded to the other and this to the 3-N of the aurated ring, while gold(I) is linearly surrounded by one phosphorus and one sulphur atom (P–Au–S 172.0(1)°; Au–P 2.292(3), Au–S 2.330(3) Å). The family of the compounds **1–6** show a restricted range of values for the IS and QS values (3.0–3.5 and 7.8–8.4 mm sec^{-1}, respectively) showing that the S-donating ligand has only a moderate effect on them.

Compounds **7–11** constitute a second family, featuring a P–Au–N arrangement, in terms of their infrared and various NMR spectra. In the case of compound **9** [5], an X-ray crystal structure determination shows that each of the two gold(I) nuclei is linearly surrounded by one phosphorus and one nitrogen atom (P–Au–N 178.3(4)°; Au–P 2.233(5), Au–N 2.022(12) Å): the packing of discrete molecules without any Au · · · Au interaction leaves space for clathrated molecules of benzene. For this group of compounds a restricted range of IS and QS is observed: 2.7–3.3 and 8.4–8.5 mm sec^{-1} respectively.

Additional evidence for the P–Au–X (X = C, S or N) arrangement in the compounds studied here can be found in the agreement between the experimental QS values and those calculated on the basis of the partial quadrupole splitting model (Table 1) using as a working approximation the following literature values for the respective contributions [1]: -2.38 for tertiary phosphine, -1.82 (as in pyridine) for all N-ligands, -1.90 or -2.69 (as in methyl or in acetylide, respectively) for C-ligands and -1.61 mm sec^{-1} (as in –SR derivatives) for S-ligands.

The parameters in Table 1 are grouped for each family of compounds: P–Au–S (**1–6**), P–Au–N (**7–11**) and P–Au–C (**12–15**) and, inside each family, in order of increasing covalent character of the Au-ligand bonds according to the Mössbauer data. When the electron donation from the ligands towards the Au atom increases, the population of the $6s$ and $6p_z$ orbitals increases, the first effect leads to an increase in the IS value and the latter to that in the QS value, since the $6p_x$ and $6p_y$ orbitals are not occupied. A very high QS, not found for other olefin or acetylene complexes, is shown by compounds **14** and **15**, which is consistent with the absence of π-bonding in our compounds.

If the compounds containing Au–S (**1–6**) or Au–N bonds (**7–11**) are considered, it can be seen that both the IS and QS ranges are quite similar. The observed similarity between the parameters of the two classes shows that Mössbauer spectroscopy cannot be used to distinguish between S–Au–P or N–Au–P coordination nor between either of these and a C–Au–P arrangement. This is shown by the overlapping of the relevant regions (marked A, B and C respectively in Fig. 1) in the IS/QS plane; overlapping accounts for the absence of the two doublets expected for the tetra-aurated compound **13**, for which, however, the broadness of the lines (LW = 2.04 mm sec^{-1}) indicates unresolved quadrupole doublets. Although the ^{197}Au Mössbauer parameters are rather insensitive to the ligand *trans* to the phosphine ligands, they are sensitive to the change of type of carbon ligand; inspection of Fig. 1 shows that the areas marked C, D, and E relating to P–Au–C–Au–P (**12** and **13**), P–Au–C≡C (**14** and **15**) and P–AuC(aryl) are well separated.

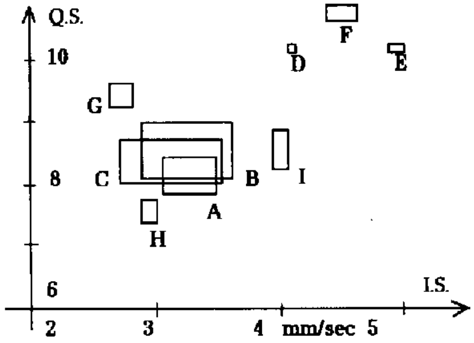

Fig. 1. Areas defined by the Mössbauer parameters IS and QS according to the type of Au^I compounds investigated; data from Table 1 and from Ref. 3.

The same high sensitivity of the ^{197}Au parameters to the type of carbon ligand is found also for other compounds, e.g. $[C–Au–C]^+$ (areas F for C = isocyanide and G for C = carbene), C–Au–Cl (area H for C = carbene) or $\{\mu\text{-}[RN{=}C(OR')]Au\}_3$ (area I) [3].

Experimental

The compounds were made by published methods, as detailed in Table 1, and their identities were checked by C, H, N analysis, m.p. determinations, and comparison of the infrared and proton NMR spectra with those for authentic samples.

The ^{197}Pt activity feeding the 77.3 keV Mössbauer transition was produced by irradiation of enriched ^{196}Pt metal. Both source and absorber were kept at 4.2 K, and a sinusoidal velocity waveform and an intrinsic Ge detector were used. The shifts are relative to the Au(Pt) source. Depending upon the compound, a sample of the absorber with a ^{197}Au of ca. 50 mg cm^{-2} was used. The spectra were recorded for various Q–Au–PR_3 compounds having a S–AuP (**1**–**6**), N–AuP (**7**–**11**) or C–AuP (**12**–**15**) bond. The relevant Mössbauer parameters, namely IS, QS and LW (i.e. isomer shift, quadrupole splitting and average half-width, respectively) are reported in Table 1. All the spectra show only one resolved quadrupole doublet. Nearly all the linewidths are close to the minimum value (1.89 mm sec^{-1}) in agreement with the presence of only one detectable gold state. The relatively broad line observed for compound **7** is probable due to decomposition of the sample as a result of prolonged standing or irradiation; in this case a fitting procedure with two doublets was unsuccesfully attempted.

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References

1 R.V. Parish, Gold Bull., 15 (1982) 51; H. Schmidbaur, in Gmelins Handbuch der Anorganischen Chemie, Springer-Verlag, Berlin, 1980; J.G. Stevens, G.H.M. Calis and L.H. Bowen, Anal. Chem., 54 (1982) 204R; R.V. Parish, Hyperfine Interactions, 40 (1988) 159.

2 M. Katada, K. Sako, Y. Uchida, S. Iijima, H. Sano, H.H. Wei, H. Sakai and Y. Maeda, Bull. Chem. Soc. Jpn., 56 (1983) 945; H. Schmidbaur, C. Hartmann and F.E. Wagner, Angew. Chem., Int. Ed. Engl., 26 (1987) 1148; L.S. Moore, R.V. Parish, R. Uson, A. Laguna, M. Laguna and F.M. Nieves, J. Chem. Soc., Dalton Trans., (1988) 23; H. Schmidbaur, G. Rebr, A. Schier, F.E. Wagner and G. Mueller, Inorg. Chim. Acta, 147 (1988) 143; J. Meyer, J. Willnecker and U. Schubert, Chem. Ber., 122 (1989) 223; D.T. Hill, G.R. Girard, F.L. McCabe, R.K. Johnson, P.D. Stupik, J.H. Zhang, W.M. Reiff and D.S. Eggleston, Inorg. Chem., 28 (1989) 3529.

3 (a) F. Bonati, A. Burini, B.R. Pietroni, S. Calogero and F.E. Wagner, J. Organomet. Chem., 309 (1986) 363; (b) G. Banditelli, F. Bonati, S. Calogero, G. Valle, F.E. Wagner and R. Wordel, Organometallics, 5 (1986) 1346; (c) F. Bonati, A. Cingolani, S. Calogero and F.E. Wagner, Inorg. Chim. Acta, 127 (1987) 87.

4 F. Bonati, M. Felici, B.R. Pietroni and A. Burini, Gazz. Chim. Ital., 112 (1982) 5; F. Bonati, A. Burini, M. Felici and B.R. Pietroni, Gazz. Chim. Ital., 113 (1983) 105; F. Bonati, A. Burini, B.R. Pietroni and M. Felici, J. Organomet. Chem., 274 (1984) 275; B. Bovio, F. Bonati, A. Burini and B.R. Pietroni, Z. Naturforsch., 39b (1984) 1747; F. Bonati, A. Burini, B.R. Pietroni and B. Bovio, J. Organomet. Chem., 296 (1985) 301; F. Bonati, A. Burini and B.R. Pietroni, Z. Naturforsch., 40b (1985) 1749; F. Bonati, A. Burini, B.R. Pietroni and E. Giorgini, Inorg. Chim. Acta, 137 (1987) 81; F. Bonati, A. Burini, B.R. Pietroni and B. Bovio, J. Organomet. Chem., 375 (1989) 147.

5 F. Bonati, A. Burini, B.R. Pietroni and B. Bovio, J. Organomet. Chem., 317 (1986) 121.

6 F. Bonati, A. Burini, B.R. Pietroni, E. Giorgini and B. Bovio, J. Organomet. Chem., 344 (1988) 119.

7 T. Amagai, T.K. Miyamoto, H. Ichida and Y. Sasaki, Bull. Chem. Soc. Jpn., 62 (1989) 1078.

8 C.K. Mirabelli, D.T. Hill, L.F. Faucette, F.L. McCabe, G.R. Girard, D.B. Bryan, B.M. Sutton, J.O.L. Barus, S.T. Crooke and R.K. Johnson, J. Med. Chem., 30 (1987) 2181.