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A GOLD-197 MÖSSBAUER INVESTIGATION OF VARIOUS GOLD(I) DERIVATIVES OF FIVE- OR SIX-MEMBERED NITROGEN-CONTAINING HETEROCYCLES

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Summary

The Mössbauer spectra of (triphenylphosphine)AuQ (QH is an imidazole, 2-pyridone, or theobromine), of 2-phenylimidazolylgold(I), and of 1-phenyl-3-methyl-4,4′-bis(triphenylphosphinegold)pyrazolone-5 are reported and discussed. Comparison with the available data, including X-ray crystal structures, shows that ^{197}Au spectroscopy is 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.

Introduction

During our investigation of the gold derivatives of azoles [1,2], azolones [3], pyrimidines and purines [4], several compounds were isolated which contained Au–C, Au–N, or Au–P bonds. In a few cases X-ray crystal structure determinations confirmed the formulae proposed, but this technique could not always be used because of the lack of suitable crystals. Such an occurrence is not rare in the field of gold chemistry; for example no X-ray crystal structure determination has been reported for the established chrysotherapeutic agents sodium gold thiomalate, "Myocrisine", or gold thioglucose, "Solganol". In view of this recourse has to be made to ^{197}Au Mössbauer spectroscopy, and we now discuss our results for some gold(I) azolates together with data from the literature [5,6].

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Results and discussion

The Mössbauer parameters, such as isomer shift, IS, quadrupole splitting, QS, and average half-width of the line, LW, are listed in Table 1 together with pertinent literature data. The Mössbauer spectrum of each of our compounds (see Fig. 1) consists of a single doublet whose parameters, typical of gold(I), can be divided into three families, each of which corresponds to a suggested coordination pattern around the gold atom.

For the compounds listed in Table 1 the ratio QS/IS is fairly constant, thus showing the linear correlation between these values typical of linear two-coordinated gold(I) complexes. If the covalent character of the Au–ligand bonds is increased, then both electron donation from the ligand towards the metal and population of the 6*s* and 6p_z increase. The first effect leads to an increase in the IS values (since $\Delta R/R$ is positive for gold), while the second leads to an increase in the

TABLE 1

^{197}Au PARAMETERS AT 4.2 K

Compound [a]	IS [b,c]	QS [b]	QS [b,d]	LW [b,e]	Ref.
1st family: P–Au–N					
1-(LAu)imidazole (**1**)	3.51(1)	8.93(1)	−8.40	1.95(2)	1
1-(LAu)benzimidazole (**2**)	3.57(1)	8.95(1)	−8.40	1.92(2)	2
1-(LAu)-2-iso-propylimidazole·0.5 benzene (**3**)	3.53(2)	8.95(2)	−8.40	1.94(3)	7
1-(LAu)benzotriazole (**4**)	3.15(4)	8.32(4)	−8.40	2.04(4)	5
1-(LAu)-3,5-dimethylpyrazole (**5**)	3.55(4)	9.00(4)	−8.40	1.95(4)	5
1-(LAu)theobromine (**6**)	2.97(2)	8.25(2)	−8.40	1.86(6)	4
1-(LAu)pyridone-2 (**7**)	2.96(1)	8.18(1)	−8.40	1.85(3)	14
2nd family: N–Au–N					
1-Au-2-phenylimidazole (**8**)	2.35(2)	7.63(2)	−7.28	2.10(5)	15
1-Au-pyrazole (**9**)	2.18(4)	7.35(4)	−7.28	2.11(4)	5,8
1-Au-3,5-dimethylpyrazole (**10**)	2.05(4)	7.39(4)	−7.28	2.37(4)	5,8
Au_3(pyrazolato)$_3I_2$ [f] (**11**)	2.17(4)	7.43(4)	−7.28	2.18(4)	5,8
Au_3(3,5-dimethylpyrazolato)$_3I_2$ [f] (**12**)	2.34(4)	7.82(4)	−7.28	2.23(4)	5,8
3rd family: (i) P–Au–C					
LAuPh (**13**)	4.98(4)	10.24(4)	−10.36	2.50(4)	6
LAu(*p*-tolyl) (**14**)	4.90(4)	10.15(4)	−10.36	2.80(4)	6
LAu (fc) (**15**)	4.82(4)	10.18(4)	−10.36	2.04(4)	6
3rd family: (ii) P–Au–C–Au–P					
[$(LAu)_2$Ph]BF_4 (**16**)	3.05(4)	8.48(4)	−10.36	2.46(4)	6
[$(LAu)_2$(*p*-tolyl)]BF_4 (**17**)	2.85(4)	8.18(4)	−10.36	2.60(4)	6
[$(LAu)_2$(fc)]BF_4 (**18**)	2.70(4)	8.07(4)	−10.36	2.44(4)	6
1-Ph-3-Me-4,4′-$(LAu)_2$-pyrazolone-5 (**19**)	3.52(4)	8.96(4)	−10.36	1.95(13)	3

[a] L means triphenylphosphine, fc ferrocenyl. [b] In mm s^{-1}. [c] Reference to Pt/Au source. [d] Values calculated according to the point charge model. [e] Average value. [f] Values of the gold(I) sites.

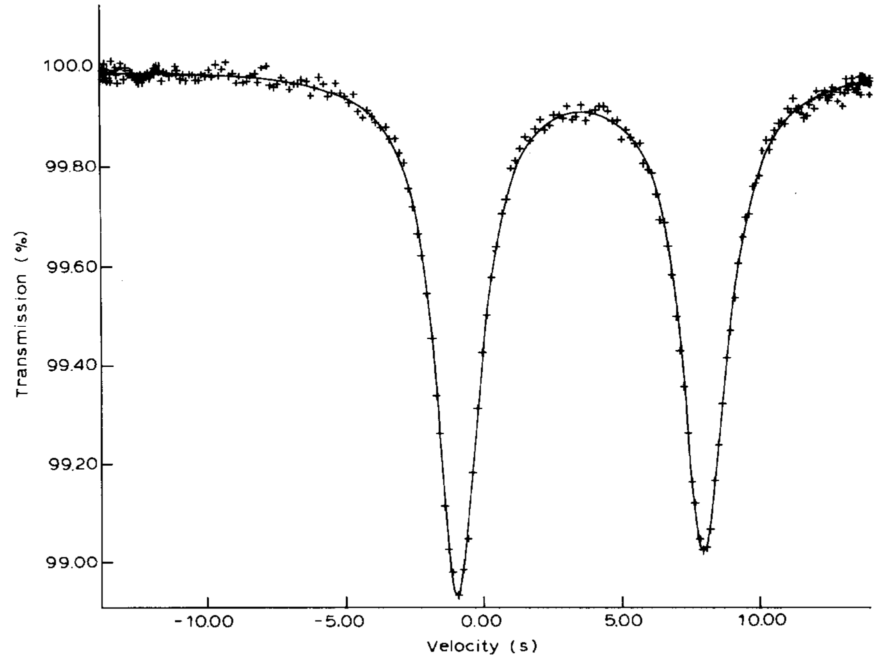

Fig. 1. Mössbauer spectrum of triphenylphosphinegold(I) imidazole (compound **1** in Table 1).

QS values, since the $6p_x$ and $6p_y$ orbitals are unoccupied. In our compounds the electrical field gradient arises from the $6p_z$ population, so that the signs of all the QS values listed in Table 1 are negative because the quadrupole moment of the ^{197}Au nuclear ground state is positive.

The first family (compounds **1**–**7**) contains a P–Au–N arrangement; it is characterized by IS and QS values within restricted ranges, 2.9–3.6 and 8.1–9.0 mm s^{-1}, respectively. In this family linear coordination around the gold nucleus was established by X-ray crystal structure determination carried out on the compound **3** [7] and on 1-(triphenylphosphinegold)-6-methyl-pyridone-2 [14], a methylated homologue of **4**; in both cases no Au · · · Au interaction was found. Within the family it is evident from the data relating to the compounds **1**, **2**, **3** and **5** that substitution on the imidazole ring (benzoimidazole, 2-iso-propylimidazole) or replacement of this ring by the isomeric pyrazole ring, has no net effect on the Mössbauer parameters. On the other hand, moderate but significant effects are evident when the ring is altered either by replacement on a CH by a nitrogen atom (benzimidazole vs. benzotriazole derivative, compound **2** and **4** respectively) or by introduction of electronegative substituents, such as one or two carbonyl groups (e.g. 2-pyridone or theobromine derivative, **7** or **6** compared with **1** and **2**, respectively).

The various components of the second family (compounds **8**–**12**) contain a N–Au–N arrangement; they, too, are characterized by a restricted IS and QS range, namely 2.0–2.3 and 7.4–7.8 mm s^{-1}, respectively. No X-ray crystal structures are available for the compounds because they are either insoluble coordination oligomers or polymers (**8**–**10**), or revert to pyrazolylgold(I) and iodine when a crystallization is attempted (**11**, **12**). However, for analogous compounds with carefully chosen substituents on the heterocyclic ring, mass spectroscopic and osmometric measurements [8] showed that some of the pyrazolylgold(I) species are cyclic trimers. Moreover, in the case of tris(3,5-bis(trifluoromethyl)pyrazolato-*N*,*N*′)trigold(I) [9] an X-ray crystal structure determination confirmed that the molecule does, indeed, contain a nine-membered ring and three linear N–Au–N groups. The Mössbauer spectra of such trimeric molecules each consists of a single doublet, indicating that the three gold atoms inside the ring are identical, and that no significant Au · · · Au inter- or intra-molecular interaction can be detected within the resolution allowed by Mössbauer spectroscopy.

In the third family there are various molecules (**13**–**19**) in which the gold atom is flanked by a triphenylphosphine and by an organic group. It should be noted that the compounds **13**–**15** are characterized by a single P–Au–C arrangement, while the remaining compounds contain a P–Au–C–Au–P moiety, as revealed by the X-ray crystal structure of compound **17** [10]. Correspondingly, the Mössbauer parameters for the former group fall in one range (IS 4.8–5.0, QS 10.1–10.3 mm s^{-1}), and those for the compounds **16**–**18** in another range (IS 2.7–3.1, QS 8.0–8.5 mm s^{-1}). When the two groups **13**–**15** and **16**–**18** are compared, a change of values in both IS and QS is expected because a terminal aryl or ferrocenyl ligand present in the former group has become bridging owing to the formation of a three-center two-electron bond between the two gold and the bridging carbon atoms. Such a bond is not at all likely in compound **19**, which, nevertheless, contain a P–Au–C–Au–P arrangement. Therefore the expected IS and QS values for this compound should be intermediate between the two ranges, but more on the side of the binuclear compounds, as was found (IS 3.52, QS 8.96 mm s^{-1}).

The use of the partial quadrupole splitting (pqs) model [11] to rationalize the electrical quadrupole splitting of the gold(I) compounds may be open to question because of the *s*–*p* rehybridization effects resulting from *trans*-influence. Nevertheless we do use pqs model here to rationalize the quadrupole splitting data for linear gold(I) coordination. To this end a pqs value of -2.38 mm s^{-1} is used for triphenylphosphine; then, as a working approximation, a value of -1.82 mm s^{-1} (i.e. the value of pyridine) is assigned to all the *N*-bonded ligands present in Table 1; finally the value of -2.80 mm s^{-1} (i.e. the value of methyl) is assigned to all the *C*-bonded ligands present in Table 1, where the QS values calculated upon these assumptions are listed. The agreement between observed and calculated QS values are satisfactory for all the compounds belonging to the first or second family, as are those of the first part (i) of the third family, in full agreement with the presence of a linear coordination around the gold(I) atom in the species **1**–**15**. On the other hand there is no agreement between calculated and experimental QS values in the case of the second part of the third family, i.e. compounds **15**–**19**. The origin of this deviation is probably connected with the presence in these molecules of a carbon atom bonded to two gold atoms rather than to the effect of a possible Au · · · Au interaction, especially since it has previously been shown that such interactions have no marked influence on Mössbauer parameters [12].

It is evident from the results that parameters obtained from ^{197}Au Mössbauer spectroscopy can give useful information about the coordination around a gold(I) nucleus in a solid compound for which an X-ray single crystal diffraction is impossible.

Experimental

The samples were prepared by the literature methods referred to in Table 1. Their identities and purities were checked by C,H,N analyses, melting point determinations, and infrared spectra. The IR spectrum was recorded again after the Mössbauer spectrum in each case, and no change was observed.

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 reported shifts are relative to the Au(Pt) source. Depending upon the compounds a sample of the absorber with a ^{197}Au content of 50–200 mg cm^{-2} was used. Some of the isomer shift data taken from the literature were converted to this scale by using the value given in ref. 13. A typical Mössbauer spectrum is shown in Fig. 1.

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