ESCA and Mössbauer Study of Compounds of Gold in the Oxidation States +I, +II, and +III

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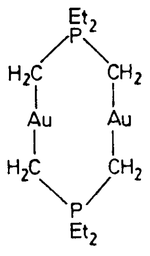
Summary ESCA and ^{197}Au Mössbauer spectra of a series of ylide complexes of Au^{I}, Au^{II}, and Au^{III} have been recorded; the results show significant trends in the various parameters and a correlation between ESCA and Mössbauer data appears to exist.

TABLE 1 Core level binding energies (eV) of gold compounds[a]

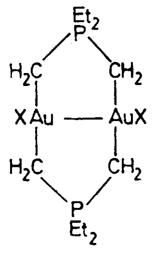
Sample	Au($4f_{7/2}$)	Cl ($2p_{3/2}$)/Br ($3p_{3/2}$)	C($1s$)	P($2p_{3/2}$)/As ($3p_{3/2}$)	K($2p_{3/2}$)
(**1**)	84·55		285·32	131·94	
(**2a**)	86·41	198·52	285·32	132·32	
(**2b**)	86·44	182·82 (Br)	285·32	132·47	
(**3**)	86·96	182·66 (Br)	285·32	132·79	
Ph_3PAuCl	85·55	198·50	284·85	131·73	
$Ph_3AsAuCl$	85·08	198·10	284·85	43·39 (As)	
$KAuCl_4$	87·59	198·10	285·32		292·35

[a] The ESCA spectra were taken with a Hewlett–Packard 5945 spectrometer. The binding energies for sample (**1**) were calibrated *vs.* the Au($4f_{7/2}$) line of a gold dot evaporated onto the surface of the sample. Alkyl C($1s$) was then found at 285·32 eV. All other compounds were referenced against their C($1s$) signal, which was assumed to be also at 285·32 eV. The binding energies are therefore relative, but internally consistent values.

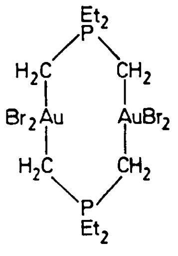
RECENTLY a series of organogold compounds in which Au^{1+} and Au^{3+} as well as Au_2^{4+} centres are linked by novel ylidic ligands has been reported.[1,2] As has been confirmed by *X*-ray results[2] the diatomic Au_2^{4+} unit contains gold in the rare +II oxidation state. In order to facilitate the detection and identification of this state in other compounds of Au^{II}, it is desirable to obtain further characteristic data. As part of more extensive programs in the fields of ESCA[3] and Mössbauer[4] spectroscopy the set of three complexes



(1)



(2) a; X = Cl
b; X = Br



(3)

μ-bis(diethylphosphoniodimethylene)-digold (**1**), μ-bis(diethylphosphoniodimethylene)-bis(chlorogold)(*Au–Au*) and -bis(bromogold)(*Au–Au*) (**2a** and **b**), and μ-bis(diethylphosphoniodimethylene)-bis(dibromogold) (**3**), as well as some reference compounds were investigated by these two techniques. The results are summarized in Tables 1 and 2. The Mössbauer spectra are shown in the Figure.

TABLE 2. ^{197}Au Mössbauer data obtained at 4·2 K for ylide complexes of Au^I (**1**), Au^{II} (**2b**), and Au^{III} (**3**), and other Au complexes. The isomer shift *S* is given relative to the source of ^{197}Pt in Pt metal. ΔE_Q is the separation of the quadrupole doublet.

Sample	S/mm s^{-1}	ΔE_Q/mm s^{-1}
(**1**)	+3·76 (4)	9·60 (10)
(**2b**)	+2·67 (3)	6·71 (6)
(**3**)	+2·02 (2)	5·52 (5)
Ph_3PAuCl	+2·96 (7)[a] +2·83 (3)	7·47 (13)[a] 7·34 (7)
$Ph_3AsAuCl$	+2·76 (6)	7·40 (10)
$KAuCl_4$	+0·81 (3)[b] +0·44 (6)[c]	1·11 (6)[b] 1·27 (8)[c]

[a] From ref. 8. [b] From ref. 6. [c] From ref. 7.

The ESCA data reveal a pronounced influence of the Au oxidation state on the Au ($4f_{7/2}$) binding energies. The values differ within the series of compounds by as much as 2·6 eV, the trend being in good agreement with theoretical predictions.[5] The differences obtained are large enough to distinguish between the various oxidation states of gold. The difference between compounds with Cl and Br ligands, on the other hand, amounts to only slightly more than the

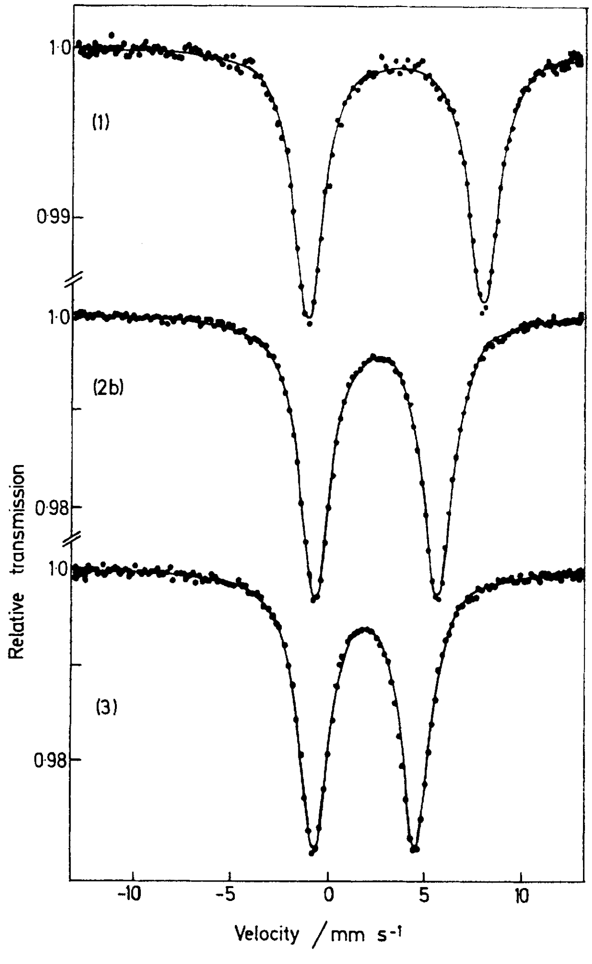


FIGURE. ^{197}Au Mössbauer spectra of some ylide complexes of Au^I (top), Au^{II} (centre), and Au^{III} (bottom), taken at 4·2 K with a source of ^{197}Pt in Pt metal.

standard experimental error of ± 0·1 eV. The effects of the Au oxidation state on the C(1s), P($2p_{3/2}$), and Br($3p_{3/2}$) energies are also negligibly small.

The ^{197}Au Mössbauer spectra of the ylide complexes show a systematic decrease of the isomeric shift with increasing Au oxidation state. This trend is reminiscent, for instance, of the behaviour of the $KAu(CN)_2$ and $KAu(CN)_2Br_2$ or Ph_3PAuCl and Ph_3PAuCl_3 pairs. In these cases, the Au^{III} complexes also yield smaller isomer shifts than their Au^{I} counterparts.[6–8] For pure halides, however, one finds the opposite behaviour, *i.e.* a monotonic increase of the isomer shift with the Au oxidation state.[6–9] The Mössbauer isomer shift(s) and quadrupole splitting (ΔE_Q) data for the Au^{I} (**1**) and Au^{III} (**3**) ylide complexes are in good agreement with the established S–ΔE_Q correlations[6–8] for gold compounds.

A detailed interpretation of the correlation between the Mössbauer isomer shifts and the Au($f_{7/2}$) core electron binding energies found for this set of three ylide complexes has to await a broader range of experimental evidence. Nevertheless, it is clear that Mössbauer data may contribute to the elucidation of unknown oxidation states in a given series of compounds.

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