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^{197}Au-Mössbauer Spectroscopic Studies of Gold Compounds

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^{197}Au Mössbauer effect measurements of mixed-valence compounds and chelates of Au(III) with ligands of 1,10-phenanthroline, 8-quinolinol, and their derivatives have been carried out. The Mössbauer data of $Cs_2Au_2Cl_6$, $Cs_2AgAuCl_6$, and [Au(phen)Cl_2]Cl show the existence of an interaction between metal atoms through Cl atoms. Although the metal-metal interaction in [Au(Hdmg)$_2$][AuCl_2] has been postulated by X-ray study, no such interaction was observed. Two kinds of 8-quinolinol Au(III) complexes which have *cis-trans* isomers are assigned to the compounds of the [Au(oxine)$_2$][AuCl_4] and [Au(oxine)Cl_2] types.

Mössbauer spectroscopy has been widely used to study the nature of chemical bonding and the structures of inorganic and organometallic compounds, especially those of iron and tin compounds.

Although the ^{197}Au Mössbauer experiment has some disadvantages, such as the short half-life (18 h) of the source nuclide and the low recoil-free fraction, which require the use of a nuclear reactor and low-temperature measurement, the application of Mössbauer spectroscopy has recently become popular as a useful physicochemical technique because the spectrum is generally unambiguous and sensitive to the nature of chemical bonding and the structures of gold compounds.[1,2)]

The present work was carried out in order to elucidate the interaction between the two different gold atoms in different sites in the mixed-valence compounds, such as $Cs_2Au_2Cl_6$, [Au(Hdmg)$_2$][AuCl_2], and [Au(phen)-Cl_2][AuCl_4], and in order to clarify the structure of chelate complexes of Au(III) with 1,10-phenanthroline, 8-quinolinol, and their derivatives as ligands.

Experimental

$CsAuCl_4$,[3)] $Cs_2AgAuCl_6$,[3)] [Au(Hdmg)$_2$][AuCl_2] (Hdmg= dimethylglyoximato(1-)),[4)] [Au(phen)Cl_2]Cl (phen=1,10-phenanthroline),[5)] [Au(phen)Cl_2]ClO_4,[5)] [Au(phen)Cl_2]-[AuCl_4],[5)] Au(dmp)Cl_3 (dmp=2,9-dimethyl-1,10-phenanthroline),[6)] Au(dmp)Br_3,[6)] [Au(oxine)$_2$][AuCl_4] (oxine=8-quinolinol),[7)] and [Au(oxine)Cl_2][7)] were prepared by the methods described in the literature. Thermal decomposition product of $CsAuCl_4$, $Cs_2Au_2Cl_6$(dec) was prepared by a method similar to that of Brauer and Sleater[8)] by checking the decomposition process by TGA and DSC. Another sample of $Cs_2Au_2Cl_6$(syn) was prepared directly by heating the stoichiometric mixture of CsCl, Au, and $CsAuCl_4$ in an evacuated quartz tube at 450 °C for one week and then cooling it rapidly in water. The crystal thus obtained was annealed at 250 °C for 3 d.

[Au(5-Cl-oxine)Cl_2] (5-Cl-oxine=5-chloro-8-quinolinol) was prepared by a method similar to that used in the preparation of 8-quinolinol gold complexes.[7)] The purity of the samples was checked by elemental analysis and powder X-ray diffractometry (Cu $K\alpha$ radiation).

^{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 by a pure-Ge diode detector. The data were stored in a microcomputerized multichannel analyser constructed by Uehara and Maeda.[9)] A ^{197}Pt source was made by irradiating a 100-mg disk of metallic Pt enriched to 98% in ^{196}Pt. The velocity scale was calibrated by taking the spectrum of an iron foil against a ^{57}Co(Pt) source, both at room temperature. The spectra were fitted with Lorentzian line shapes by using the least-squares fitting program. The precision of the Mössbauer parameters obtained is within ±0.04 mm/s for single component spectra and ±0.08 mm/s for double component spectra. All the isomer shift data are referred to the Au-metal resonance at 18 K.

Results and Discussion

$CsAuCl_4$, $Cs_2Au_2Cl_6$(syn), $Cs_2Au_2Cl_6$(dec), and $Cs_2AgAuCl_6$. Some typical Mössbauer spectra of $CsAuCl_4$, $Cs_2Au_2Cl_6$(syn), and $Cs_2AgAuCl_6$ are shown in Fig. 1. Table 1 summarizes the Mössbauer parameters, isomer shift (*IS*), quadrupole splitting (*QS*), and half-width (Γ_{exp}) derived from the observed spectra. The isomer shift and quadrupole splitting of $CsAuCl_4$ are similar to those of the compounds containing discrete square-planar-complex ions, $[AuCl_4]^-$.[10,11)] This indicates that gold atoms are coordinated essentially in the square-planar form and that the isolated $[AuCl_4]^-$ ion exists in a solid. The complicated spectra of both the

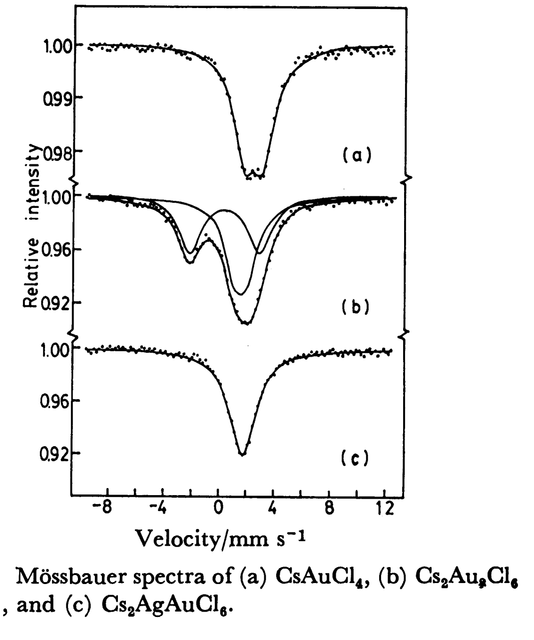

Fig. 1. Mössbauer spectra of (a) $CsAuCl_4$, (b) $Cs_2Au_2Cl_6$ (syn), and (c) $Cs_2AgAuCl_6$.

TABLE 1. MÖSSBAUER DATA OF CESIUM GOLD CHLORIDES AND CECIUM SILVER GOLD CHLORIDE

Compound	IS / mm s^{-1}	QS / mm s^{-1}	Γ_{exp} / mm s^{-1}
$CsAuCl_4$	2.16	1.37	1.96
$Cs_2Au_2Cl_6$(syn)			
Au(I)	0.13	5.06	2.04
Au(III)	1.31	1.00	1.88
$Cs_2Au_2Cl_6$(dec)			
Au(I)	0.23	5.25	1.89
Au(III)	1.56	0.95	2.00
$Cs_2AgAuCl_6$	1.54	—	2.33

$Cs_2Au_2Cl_6$(dec and syn) samples suggest the presence of two or more different sites or oxidation states for the gold atom in these compounds. The crystal structure of $Cs_2Au_2Cl_6$ was determined first by Elliot and Pauling from powder X-ray diffraction data.[12]

According to their results, this compound contains complex ions of linear $[AuCl_2]^-$ and square-planar $[AuCl_4]^-$ units, and they postulated the possibility of interaction between Au(I) and Au(III) sites through Cl atoms. In recent years, however, the structure was redetermined by using single crystal data by Tindermans-v. Eijindhoven and Verschoor.[13] They pointed out that there was no interaction between Au(I) and Au (III) atoms through Cl atoms. In Fig. 1(b), the outer doublet is assigned to the Au(I), and the inner doublet to the Au(III). The slight differences in Mössbauer parameters between the two samples (syn and dec), and between ours and those reported by Faltens and Shirley,[10] may be due to the different preparation process and/or an error in the deconvolution of the spectra. In the work by Faltens and Shirley, $Cs_2Au_2Cl_6$ was prepared from an acid solution of CsCl and AuCl. The values of IS for Au(III) in both $Cs_2Au_2Cl_6$ (syn) and $Cs_2Au_2Cl_6$ (dec) are smaller than that of $CsAuCl_4$ and those of some compounds containing a discrete $[AuCl_4]^-$ ion. Unfortunately, Faltens and Shirley did not interpret the correlation of the Mössbauer parameters with the structures of $Cs_2Au_2Cl_6$. If the postulation of Elliot and Pauling were correct, the configuration around the Au(III) atom in the $[AuCl_4]^-$ site should be a distorted octahedron with four Cl atoms of the $[AuCl_4]^-$ ion and two additional Cl atoms from adjacent $[AuCl_2]^-$ ions, as is shown in Fig. 2. In this case, it would be impossible to form six equivalent $5d^26s6p^3$ hybrid bonds involving the promotion of two electrons. The formation of six equivalent bonds using a $5d6s6p^36d$ hybridization also seems to be unlikely from the point of view of energy. However, the formation of an octahedron elongated to the z-axis (normal to the square plane of $[AuCl_4]^-$) with six Cl atoms, may be explained by assuming that two 6p6d hybrid bonds are added to the $5d6s6p^2$ hybrid bonds which hold the four Cl atoms in square-planar form. The additional co-linear 6p6d hybrid bonds should be elongated in the direction of the z-axis because of the repulsion of the filled $5d_z$ gold orbital in the gold atom. This explanation was suggested by Sutton to interpret hexa-coordinated Au(III) ions, such as $[Au(diars)_2I_2]^+$ (diars $=$ *o*-phenylenbis(dimethylarsine)) and $[AuBr_6]^{3-}$.[14,15] The additional electrons of the 6p6d hybrid orbital may be expected to decrease the isomer shift because of the increased shielding effect of p- and d-electrons on s-electrons.

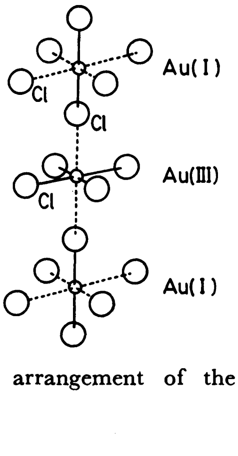

Fig. 2. Stacking arrangement of the $[AuCl_4]^-$ and $[AuCl_2]^-$ units.

The IS value of the Au(I) site is considerably smaller than that of the corresponding Au(I) chloride, $(C_6H_5)_4AsAuCl_2$ ($IS=1.72$ mm/s and $QS=6.13$ mm/s).[16] Au-atoms are also surrounded by six Cl atoms and form a contracted octahedron, as is shown in Fig. 2.

The additional four bonds may be formed by using $6p^26d^2$ hybridization; hence, the s-electron density decreases as a result of the increased shielding effect of p- and d-electrons, as in the case of Au(III).

The decreasing tendency of QS values for Au(I) and Au(III) sites also supports the hexa-coordinated structure of gold atoms. As is known in the case of covalent square-planar Au(III) compounds where Au (III) uses the $5d_{x^2-y^2}$, 6s, $6p_x$, and $6p_y$ orbitals, the occupation of these orbitals will cause a positive contribution to the electric field gradient (EFG), while a nonbonding $5d_{z^2}$ orbital will produce a negative contribution to the EFG. By assuming that the EFG of the original $[AuCl_4]^-$ site is positive, it may be concluded that the increase in electron densities along the z-axis as a result of 6p6d hybridization produces a negative contribution to the EFG, so that the total EFG becomes smaller. For linear Au(I) compounds, the z-axis is taken along the molecular axis and 6s6p hybrid orbitals of gold are used as σ-bonds. This has been confirmed experimentally for $K[Au(CN)_2]$, in which the EFG value for linear Au(I) compounds is negative.[17] Since four additional Au–Cl bonds, using the $6p^26d^2$ hybrid orbitals, produce a positive contribution to the EFG, the total EFG can be expected to decrease.

The crystal structure of $Cs_2AgAuCl_6$ is known to be the same as that of $Cs_2Au_2Cl_6$. From the discussion presented above of Mössbauer parameters of $Cs_2Au_2Cl_6$, the unresolved quadrupole splitting found on $Cs_2AgAuCl_6$ can be explained as follows: the positive and negative contributions to the EFG are almost equal, so that the effective EFG becomes zero or negligible. This result suggests that there is a strong interaction between Ag(I) and Au(III) sites through Cl atoms. The existence of such a strong interaction between the metal atoms in $Cs_2AgAuCl_6$ has also been pointed out by Yamada and Tsuchida from the dichroism measurement of this

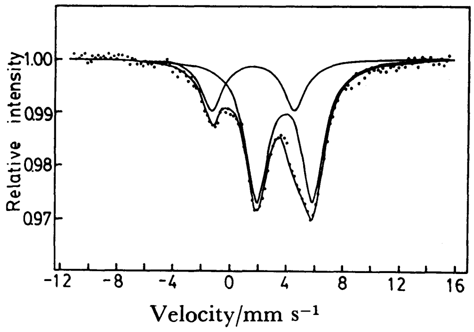

Fig. 3. Mössbauer spectrum of [Au(Hdmg)$_2$][AuCl$_2$].

Table 2. Mössbauer data of [Au(Hdmg)$_2$][AuCl$_2$]

Compound	IS / mm s^{-1}	QS / mm s^{-1}	Γ_{exp} / mm s^{-1}
[Au(Hdmg)$_2$][AuCl$_2$]			
Au(I)	1.58	6.03	1.74
Au(III)	3.88	4.04	2.03

compound.[3] The present data also support their conclusion that the interaction between two metal atoms in Cs$_2$AgAuCl$_6$ is stronger than that in Cs$_2$Au$_2$Cl$_6$.

[Au(Hdmg)$_2$][AuCl$_2$]. The Mössbauer spectrum and the derived parameters of [Au(Hdmg)$_2$][AuCl$_2$] are shown in Fig. 3 and in Table 2, respectively. Rundle determined the structure of this compound and postulated the existence of a direct interaction between the Au(I) and Au(III) atoms.[4] However, the fact that the values of *IS* and *QS* for the Au(I) site are similar to those of the isolated [AuCl$_2$]$^-$ ion in [(C$_6$H$_5$)$_4$As]-[AuCl$_2$] indicates no metal-metal interaction between Au(I) and Au(III) atoms.

This result is consistent with the results of dichroism measurement obtained by Yamada and Tsuchida.[18] The values of *IS* and *QS* for Au(III) in the [Au(Hdmg)$_2$]$^+$ ion are larger than those of the [AuCl$_4$]$^-$ ion. If the 5d6s6p^2 hybrid orbitals are used to form a square-planar form, this difference can be explained by the stronger σ-donating power of the Hdmg ligand compared to the Cl ligand, because the increased σ-donation by the ligand to the 6s orbital increases the s-electron density, and hence the isomer shift. At the same time, the EFG will increase as a result of the donation to the 6p$_X$ and 6p$_Y$ orbitals. Therefore, the values of *IS* and *QS* depend mainly on the σ-donating character of the Hdmg ligand, which is estimated to lie between those of the N$_3^-$ and CN$^-$ ligands, this is consistent with the estimation based on the spectrochemical series of ligands.

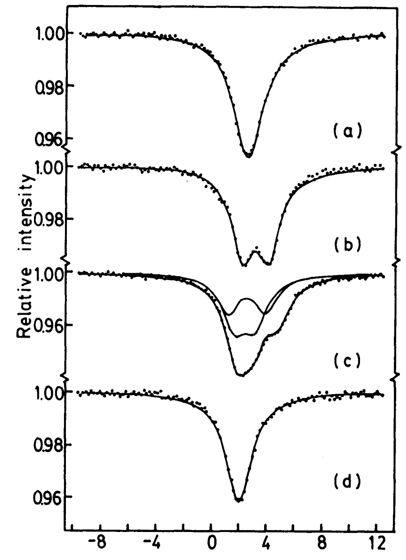

Fig. 4. Mössbauer spectra of (a) [Au(phen)Cl$_2$]Cl, (b) [Au(phen)Cl$_2$]ClO$_4$, (c) [Au(phen)Cl$_2$][AuCl$_4$], and (d) Au(dmp)Cl$_3$.

Table 3. Mössbauer data of 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline Au(III) complexes

Compound	IS / mm s^{-1}	QS / mm s^{-1}	Γ_{exp} / mm s^{-1}
[Au(phen)Cl$_2$]Cl	2.39	—	2.66
[Au(phen)Cl$_2$]ClO$_4$	3.01	1.95	2.06
[Au(phen)Cl$_2$][AuCl$_4$]			
[Au(phen)Cl$_2$]$^+$	3.33	2.74	1.97
[AuCl$_4$]$^-$	2.24	1.53	2.13
Au(dmp)Cl$_3$	1.87	—	2.31
Au(dmp)Br$_3$	2.07	—	2.76

[Au(phen)Cl$_2$]Cl, [Au(phen)Cl$_2$]ClO$_4$, [Au(phen)Cl$_2$][AuCl$_4$], Au(dmp)Cl$_3$, and Au(dmp)Br$_3$. The Mössbauer spectra of [Au(phen)Cl$_2$]X (X=Cl, ClO$_4$, and AuCl$_4$) and Au(dmp)Cl$_3$ are shown in Fig. 4. The Mössbauer parameters of these complexes are summarized in Table 3, together with those of Au(dmp)Br$_3$. The values of *IS* and *QS* for [Au(phen)Cl$_2$]Cl, [Au(phen)Cl$_2$][AuCl$_4$] and Au(dmp)Cl$_3$ are in good agreement with those reported by Takeda *et al.*[19] [Au(phen)Cl$_2$]Cl and Au(dmp)X$_3$ (X=Cl or Br) show spectra consisting of a single broad line with unresolved quadrupole splitting. This suggests that the structures of these complexes are different from the square-planar structure which is to be expected for a number of Au(III) chelate compounds. The smaller value of *IS* for [Au(phen)Cl$_2$]Cl, compared with those for [Au(phen)Cl$_2$]ClO$_4$ and [Au(phen)Cl$_2$][AuCl$_4$], also supports a gold atom with a coordination number beyond four.

Harris has investigated the structure of the 1,10-phenanthroline complexes of Au(III) halides by

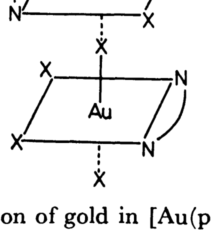

Fig. 5. Coordination of gold in [Au(phen)X$_2$]X.

conductance and spectral measurements in nonaqueous solvents.[5] From the molecular conductivities of the complexes, [Au(phen)X_2]X (X=Cl or Br), he has suggested that those complexes have a polymeric structure, in which there are two elongated gold-halogen bonds normal to the square-planar [Au(phen)-X_2]$^-$ ion, as is shown in Fig. 5. Two additional elongated Au–X bonds have been explained by assuming a colinear 6p6d hybrid bond. In accordance with his conclusion, the present Mössbauer results of [Au(phen)-Cl_2]Cl can also be explained by the consideration described in the case of $Cs_2AgAuCl_6$.

On the other hand, the quadrupole splitting is clearly observed for [Au(phen)Cl_2]ClO_4 and the *IS* is higher than that of [Au(phen)Cl_2]Cl, both indicating little or no interaction between the Au atoms in the [Au-(phen)Cl_2]$^+$ ion and the counter anion, ClO_4^-. The rather complicated Mössbauer spectrum of [Au(phen)-Cl_2][$AuCl_4$] shown in Fig. 4(c) consists of two overlapped doublets. The outer doublet corresponds to the [Au(phen)Cl_2]$^+$ ion, and the inner doublet, to the [$AuCl_4$]$^-$ ion. Both the *IS* and *QS* of the [Au(phen)Cl_2]$^+$ ion in [Au(phen)Cl_2][$AuCl_4$] show the highest values among a series of [Au(phen)Cl_2]X salts. The Mössbauer parameters of the [$AuCl_4$]$^-$ ion found in [Au(phen)Cl_2]-[$AuCl_4$] are similar to those of discrete [$AuCl_4$]$^-$ ions in other compounds previously reported by several researchers.[10,11] The results indicate that the [Au-(phen)Cl_2]$^+$ cation has no effect on its counter anion [$AuCl_4$]$^-$, although the existence of metal-metal interaction in [Au(phen)Cl_2][$AuCl_4$] might be expected, as in the case of Magnus's salt, [Pt$(NH_3)_4$][$PtCl_4$], and similar complexes. Two complexes with chelating ligand 2,9-dimethyl-1,10-phenanthroline instead of 1,10-phenanthroline, Au(dmp)Cl_3 and Au(dmp)Br_3, were prepared, and their crystal structures were determined by Robinson and Sinn.[6] According to their results, these complexes have a five-coordinated structure, described as a distorted square-pyramidal structure or as an intermediate one between trigonal- and square-pyramidal. These structure are sterically hindered from forming the expected square-planar coordination as is found in 1,10-phenanthroline complexes. The smaller *IS* value compared with those of [Au(phen)-Cl_2]X (X=Cl, ClO_4, or $AuCl_4$) can be explained as follows: the structural data show that these complexes possess an approximately square-pyramidal geometry, with a weaker extra Au–N bond along the z-axis (perpendicular to the plane of the square); therefore, it is impossible to form five equivalent σ-bonds using $5d6s6p^3$ hybridization. Another possible explanation of these structures is to assume the vacant $6p_z$ orbital is used to form an extra Au–N bond, which is elongated to the z-axis due to the repulsion of the filled $5d_{z^2}$ orbital. The population in the $6p_z$ orbital decreases the s-electron density, and hence the isomer shift. The unresolved quadrupole splitting of these complexes can be interpreted by assuming that the magnitude of the negative contribution to the EFG nearly balances the positive contribution by the extra Au–N bond formation.

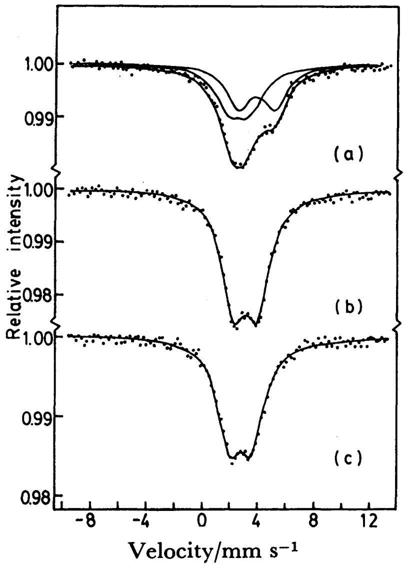

Fig. 6. Mössbauer spectra of (a) [Au$(oxine)_2$][$AuCl_4$], (b) [Au(oxine)Cl_2], and (c) [Au(5-Cl-oxine)Cl_2].

Table 4. Mössbauer data of 8-quinolinol and 5-chloro-8-quinolinol complexes

Compound	*IS* / mm s^{-1}	*QS* / mm s^{-1}	Γ_{exp} / mm s^{-1}
[Au$(oxine)_2$][$AuCl_4$]			
[Au$(oxine)_2$]$^+$	3.64	2.64	2.12
[$AuCl_4$]$^-$	2.43	1.49	2.39
[Au(oxine)Cl_2]	2.91	1.72	2.12
[Au(5-Cl-oxine)Cl_2]	2.72	1.62	2.11

[Au(oxine)$_2$][AuCl$_4$], [Au(oxine)Cl$_2$], and [Au(5-Cl-oxine)Cl$_2$]. 8-Quinolinol complexes may be used as typical examples of the diagnosis of the structure and chemical bonding of two kinds of gold chelate complexes described with the same chemical formula. The spectra of these complexes and [Au(5-Cl-oxine)Cl_2] are shown in Fig. 6, while the Mössbauer parameters are summarized in Table 4.

Two kinds of 8-quinolinol complexes, [Au$(oxine)_2$]-[$AuCl_4$] have first been prepared and explained by Inazu[7] by assuming the *cis* and *trans* isomers with respect to the coordination of oxine ligands to the central gold atom, although he did not determine which was *cis*-form or *trans*-form. One is green, and the other is amber in color. The latter complex was assigned to the compound, consisting of either a *cis* or *trans* [Au$(oxine)_2$]$^+$ cation and an [$AuCl_4$]$^-$ anion, by Inazu on the basis of paper-ionophoreisis measurements. Concerning the green-colored species, an alternative stereoisomeric cation was suggested, although no experimental information on the green-colored complex was available. We prepared these complexes according to Inazu's method and obtained green and amber-colored samples. The Mössbauer spectrum of the amber-colored complex shows the existence of two kinds of gold atoms. The present result partially confirms Inazu's conclusion, in which gold exists as both cationic and anionic species in the amber-colored compound. On the other hand, our findings for the green complex are different from the conclusion suggested by Inazu. The spectrum consisting of the doublet indicates the existence of only one kind of gold atom in its chemical state. Therefore, the formula of [Au(oxine)Cl_2] instead of [Au(oxine)$_2$][$AuCl_4$] may be appropriate for this compound. The possible structure should be square-planar, denoted as [Au(oxine)Cl_2], in view of the Mössbauer parameters. The values of *IS* for the [Au(oxine)$_2$]$^+$ ion and for the [$AuCl_4$]$^-$ ion also support the conclusion concerning the green-colored complex, [Au(oxine)Cl_2]. On the other hand, the 5-chloro-8-qunolinol ligand gives no structural isomer, and only a green complex is synthesized. As may be seen from Fig. 6, the Mössbauer spectrum for the [Au(5-Cl-oxine)Cl_2] consists of only one doublet, and the Mössbauer parameters are similar to those of the green-colored 8-quinolinol complex, [Au(oxine)Cl_2].

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