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July 1970

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STUDY OF GOLD COMPOUNDS BY NUCLEAR GAMMA RESONANCE SPECTROSCOPY

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July 1970

Abstract:

Isomer shift and electric quadrupole splitting of the 77 keV γ rays of ^{197}Au were investigated for a large number of Au(I) and Au(III) compounds at 4.2 K by nuclear gamma resonance spectroscopy (NGR). A close correlation between the observed isomer shifts and the spectrochemical series of the ligands was observed. For each oxidation state isomer shift and electric quadrupole splitting show approximately a linear relationship. On the basis of LCAO-MO theory, the experimental results are interpreted in terms of covalency effects in the molecular orbitals, synergic coupling of σ- and π- bonds, and the empirically known donor and acceptor properties of the ligands.

1. Introduction

For several years nuclear gamma resonance spectroscopy (NGR) has been

extensively used for chemical applications with compounds of iron, tin, rare

gases, rare earths and actinides[1]. Only very recently, however, this technique

has been applied to the study of compounds of 4d- and 5d- transition elements[2-6].

While a quantitative interpretation of isomer shift (IS) and electric

quadrupole splitting (QS) in complexes of heavy elements seems not to be

feasible at the present time, a correlation of experimental results with

empirical parameters may yield valuable information on chemical bonding. In

transition elements variations of IS are mainly due to the shielding of s

electrons by a varying number of d or f electrons. This is experimentally

found by the dependence of the IS on the formal oxidation state of transition

metal compounds of ^{57}Fe[7], ^{99}Ru[2], ^{193}Ir[3,4] and ^{189}Os[6], as well as theoretically

proven by the results of free-ion SCF-calculations[8-10]. On the other hand,

for compounds of Ru(II), Ru(III)[2,11], Ir[III][12] and for Fe(II) low-spin

complexes[13], a strong variation of the IS within the same formal oxidation

state was observed, suggesting a discussion of the dependence of the IS on the

nature of the ligands.

Although gold compounds are especially suited for such an investigation,

no systematic study by NGR has been published up to now[14-16]. Within the same

oxidation state, gold forms many stable complex compounds of the same symmetry

with simple ligands. Because these compounds are highly covalent, a

significant variation of the total electron density at the nucleus depending

on the type of ligand is expected.

The 77 keV M1-transition from the first excited state of ^{197}Au with spin I = 1/2$^+$ to the I = 3/2$^+$ groundstate is very well suited for this type of investigation. In the early NGR work with Au(I) and Au(III) compounds[14,15] large values for the IS compared to the linewidth of the NGR line were reported.

In the present work the IS and QS of the 77 keV γ rays of ^{197}Au were investigated for a large number of Au(I) and Au(III) compounds at 4.2 K.

2. Experiments and Results

The NGR-experiments reported here were performed in transmission geometry, with both source and absorber cooled to 4.2 K in a liquid helium cryostat. The γ rays were detected by a Ge(Li)-spectrometer. The data was stored in a multichannel analyzer operated in the multiscaler mode, the address of which was synchronously advanced with the sinusoidal motion of the source as described in Ref[17].

The ^{197}Pt sources ($T_{1/2}$ = 19h) were produced by neutron activation of natural Platinum metal foils (200 mg/cm^2 thick) and used without further preparations. When corrected for non-zero absorber thickness, the linewidths found with many absorbers are in good agreement with the natural linewidth W_o = 1.88±0.02 mm/s, deduced from the lifetime τ = 2.73±0.02 ns[18] of the 77 keV state.

Some of the transmission spectre of Au(I) and Au(III) compounds are shown in Figs. 1 and 2, respectively. A superposition of two Lorentzian lines was fitted to all spectra by a least squares procedure. The results for Au(I) and Au(III) compounds are compiled in the table. The IS is given with respect to the source of ^{197}Pt in Pt. In the last column of the table, references pertaining to synthesis or suppliers of the gold compounds are given.

Most of the spectra show a resolved electric quadrupole hyperfine splitting. The distance of the two hyperfine lines, expected for a 1/2 → 3/2 transition, is equal to the splitting

$$QS = (eQ_g \, V_{zz}/2)(1 + \eta^2/3)^{1/2}$$

of the groundstate, where $Q_g = 0.58$ b[19] is the nuclear quadrupole moment, V_{zz} the z-component of the electric field gradient tensor at the nucleus and $\eta = (V_{xx} - V_{yy})/V_{zz}$ the asymmetry parameter. The intensities of the two hyperfine components may be different due to an anisotropic Debye-Waller factor or a partial alignment of the crystallites in the absorber. Two lines with variable widths and intensities were therefore fitted to the spectra, and the IS was derived from the positions of these lines. Since the widths of both lines were in all cases found to be equal within the limits of error, their weighted average is given in column 5 of the table. In column 3 the absolute size of the electric quadrupole hyperfine splitting is given; neither the sign of QS, nor the asymmetry parameter η of the electric field gradient tensor could be derived from the data. No magnetic hyperfine interaction has been observed at 4.2 K in the investigated diamagnetic compounds, as expected.

The IS of the NGR-line is given by[21]

$$IS = \frac{2\pi}{3} Z \quad e^2 \quad \Delta |\psi(o)|^2 \quad \Delta \langle r^2 \rangle$$

where $\Delta |\psi(o)|^2$ is the difference of the total electron density at the nucleus between absorber and source and $\Delta \langle r^2 \rangle$ is the change of the mean square nuclear charge radius during the isomeric transition. A recent high-pressure NGR experiment yielded a positive value for $\Delta \langle r^2 \rangle$[22], in qualitative agreement with a weak-coupling description[23] of the first excited nuclear state of ^{197}Au.

Fig. 3 gives a graphical representation of the IS results for Au(I) and Au(III) compounds separately. For the same ligands, the ISs found for

the auric compounds are more positive than those for the aurous compounds, in

agreement with a positive sign for $\Delta \langle r^2 \rangle$ and the above mentioned d- shielding

arguments. For both oxidation states the cyanide complexes give the largest

positive isomer shifts.

In Fig. 4 QS is plotted versus IS for univalent and trivalent gold

compounds, respectively. The data clearly arrange themselves in two separate

groups according to the oxidation state, with larger quadrupole splitting

values for auric than for aurous compounds. Approximately a linear

relationship between QS and IS is found for both series of gold compounds. A

qualitative interpretation of these features will be given in the following

sections. In section 3a a correlation between the observed isomer shifts and

the spectrochemical series of the ligands is pointed out, and is interpreted

in section 3b in terms of the donor and acceptor properties of the ligands.

The observed linear relationship between QS and IS is discussed in section 3c.

3. Discussion

a) Correlation between IS and spectrochemical series of the ligands.

The IS values, plotted in Fig. 3 for aurous and auric compounds, show a large and for both oxidation states very similar variation with the type of ligand attached to the central ion. In the following a correlation between the IS and the spectrochemical series of the ligands for both univalent and trivalent gold compounds is established. In this series[24] the ligands are arranged according to increasing d-MO splitting Δ in the complex:

$$I^- < Br^- < Cl^- < \underline{S}CN^- < F^- < N_3^- < 0^{2-} < CN^-$$
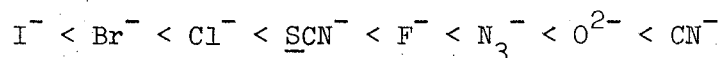
The same series has been obtained for both octahedral, tetrahedral and square planar complexes and a great number of central ions. Very probably it is also valid for transition metal complexes of other symmetries. Deviations from the given series are usually accompanied by radical changes in stereochemistry or a change in multiplicity of the central ion[25].

Au(III) compounds: Most of the auric compounds studied in this work have square planar symmetry (AuCl$_4^-$ [26], AuBr$_4^-$ [27], AuBr$_3$ [28], Au(N$_3$)$_4^-$ [29], Li$_3$AuO$_3$ [30], Au(CN)$_2$Br$_2$ [31], Au(CN)$_4^-$ [32]). The tetrafluorides, however, have a distorted octahedral structure[33].

In the square planar Au(III) complexes (microsymmetry D$_{4h}$), the metal orbitals 5d$_{x^2-y^2}$ (b$_{1g}$[†]), 5d$_{z^2}$, 6s (both a$_{1g}$) and 6p$_{x,y}$ (e$_u$) are by their symmetry suitable for σ-bonding with the ligands (which are situated on the x- and y- axes), while the metal orbitals 5d$_{xz,yz}$ (e$_g$), 5d$_{xy}$ (b$_{2g}$),

[†]Mulliken notation

$6p_z$ (a_{2u}) and $6p_{x,y}$ (e_u) can be used for π-bonding. The energetic distance

Δ_1 between the higher σ-antibonding b_{1g} (σ^*) [$5d_{x^2-y^2}$]- and the lower π-

antibonding b_{2g} (π^*) [$5d_{xy}$] – MOs is the relevant parameter of the spectro-

chemical series[34]. The data from absorption spectra of $AuCl_4^-$, $AuBr_4^-$,

$Au(SCN)_4^-$, $Au(N_3)_4^-$ and $Au(CN)_4^-$ are in agreement with the spectrochemical

series for the ligands given above[29,35,36].

The measured IS values for auric compounds (Fig. 3) increase with

increasing rank of the ligands in the spectrochemical series, with the exception

of the distorted octahedral tetrafluorides. K $Au(CN)_4$ has a comparable high

position in the IS scale as the cyanide ligand has in the spectrochemical

series of the ligands. A close spectrochemical similarity was reported for

$As(C_6H_5)_4$ $Au(N_3)_4$ [36] and K $Au(SCN)_4$ [35], which agrees with our findings of

nearly equal IS values. The IS found for K $Au(CN)_2$ Br_2 is close to an

arithmetic mean of the IS values for K $Au(CN)_4$ and K $AuBr_4$. On the other

hand, Tsuchida's "average environment" rule predicts the wavenumbers of the

ligand field bands of an octahedral complex $ML_1L_2 \ldots L_6$ with ligands L_i

as the arithmetic mean of the corresponding wavenumbers of the complexes

$M(L_i)_6$ [24]. Thus, the application of this rule to K $Au(CN)_2$ Br_2 yields a Δ_1

which is just the arithmetic mean of the Δ_1 values for the tetracyanide and

the tetrabromide, in agreement with the measured IS.

In the tetrachlorides and the oxides studied, the IS increases with the

size of the cations. Correspondingly, the ligand field splitting in tetra-

hedral Co(II) tetrahalides[37] and in Ni(II)-complexes $ANiX_3$

(A = K, Rb, Cs, pyridine; X = Cl, Br)[38] was found to increase with the size of

the cations.

Au(I) compounds: Most of the aurous compounds studied in this work are known

to contain linear L-Au-L units in the first coordination sphere of the gold

ion (AuCl [39], AuI [40], Au(N$_3$)$_2^-$ [36], AuCN [41], KAu(CN)$_2$ [42,43]). In these

diagonal Au(I) complexes (microsymmetry D$_\infty$h), the metal orbitals 5d$_z$2,

6s (both a$_{1g}$) and 6P$_z$(a$_{2u}$) are by their symmetry suitable for σ-bonding,

while the metal orbitals 5d$_{xz,yz}$(e$_{1g}$) and 6p$_{x,y}$(e$_{1u}$) have the proper symmetry

for π-bonding with the ligands, which are positioned along the z-axis. The

5d$_{xy}$, 5d$_x$2 $_-$ y2 doublet (e$_{2g}$) is nonbonding.

Again a correlation of the measured IS values with the spectrochemical

series of the ligands is noted. However, a direct experimental determination

of the d-MO splitting from optical absorption spectra is not possible in the

5d^{10} system, since all of the d-MOs are occupied. In AuCN, the gold ion is

bonded to one C and one N atom. Since the spectrochemical property of a

polyatomic ligand is usually determined by that ligand atom which is directly

bonded to the central ion[24], the average environment rule predicts for the

d-MO splitting and according to our correlation also for the IS of AuCN a

value, which is the arithmetic mean of these for KAu(CN)$_2$ and As(C$_6$H$_5$)$_4$Au(N$_3$)$_3$,

where the gold ion is bonded directly to two C- and two N- atoms, respectively.

This is in good agreement with our experimental IS values.

b) Interpretation of the correlation between IS and spectrochemical series.

In the following an interpretation of the observed correlation between

IS and spectrochemical series of the ligands is given on the basis of a cluster

LCAO-MO model.

The total electron density at the nucleus e$|\psi(o)|^2$ depends on the

chemical bondings. Positive contributions to e$|\psi(o)|^2$ arise mainly from the

atomic 6s-populations of the molecular orbitals at the gold ion (the atomic population of a LCAO-MO, as defined by Mulliken[44], is the metallic part of the total MO-population plus half of the overlap population). On the other hand, a decrease of $e|\psi(o)|^2$ is caused by the atomic 5d-populations of the MOs at the gold ion, due to the well-known shielding effect of the 5d-electrons. The atomic 6p-populations give only small contributions of both signs, a positive one by the relativistic density of $6p_{1/2}$ -electrons at the nucleus and a negative one by the shielding of s-electrons from the nucleus. From the study of optical isotope shifts in mercury it was shown that one 5d electron diminishes the total electron density at the nucleus by about 25% of the contribution of one 6s electron, while one 6p electron diminishes it only by about 10%[45]. The IS will therefore mainly depend on the atomic 6s- and 5d- populations.

The atomic population of a LCAO-MO at the metal ion is a function of the covalency parameters, which, for a given metal ion and a given symmetry, depend on the donor and acceptor properties of the ligands. In strongly covalent compounds we consequently expect a significant dependence of the IS on the donor and acceptor properties of the ligands. The absolute donor and acceptor strengths of ligands vary with the central ion, its symmetry and its oxidation state. The relative strengths, however, have approximately a universal character. Accordingly it is generally observed (for example from measurements of NMR chemical shifts[46] or of valence force constants[33]) that the σ-donor strength increases in the series $Cl^- < \underline{S}CN^- < O^{2-} < \underline{C}N^- < H^-$ [33,35].
A close proportionality between σ-donor and π-acceptor properties of a ligand was deduced from force constant measurements of Mn- and Mo- complexes[47]. This is probably a consequence of the synergic character of the metal-ligand bond,

by which a shifting of π-electron density is assumed to create a drift of

σ-electrons in the opposite direction[48]. Such a synergic coupling of σ- and

π-electrons is consistent with the electroneutrality principle.

Since the ligand field splitting in strongly covalent complexes is also

mainly determined by the donor and acceptor properites of the ligands, the

observed correlation between IS and the spectrochemical series of the ligands

can qualitatively be understood. According to Jørgensen[24] the ligand field

splitting Δ in octahedral, tetrahedral and square-planar complexes is given

by four contributions

$$\Delta = + \Delta(V) + \sigma(L \rightarrow M) - \pi(L \rightarrow M) + \pi(M \rightarrow L)$$

where the single terms are given with their proper sign. The first term

describes the splitting by the crystal-electric field, which may be neglected

in strongly covalent complexes. The following terms denote covalency effects

in σ- and π- bonding MO_s, respectively, with the direction of the electronic

charge transfer being indicated. If the atomic population of the σ-bonding

b_{1g}-MO of a square planar metal complex on the central ion increases, the

second term raises Δ_1, since the antibonding MO is destabilized. A higher

atomic population of the π-bonding b_{2g}-MO on the gold ion causes a drop in the

ligand field splitting. Delocalization of electron density from the

$b_{2g}(\pi^*)[5d_{xy}]$ - MO to empty π-ligand orbitals is taken into account through

the last term. Such a π-back bonding stabilizes the d_{π^*}-MO and hence enlarges

Δ_1. The position of a ligand in the spectrochemical series evidently increases

with increasing σ-donor and π-acceptor strength, while it decreases with π-

donor strength.

It should be noted here, that in less covalent compounds covalency is primarily determined by the energetic distance between the combining metal and ligand orbitals, i.e. in the Mulliken approximation by the difference in the orbital electronegativities[50,51]. In this case we may expect a correlation of the IS with the electronegativity series[24,50]: F < Cl ~ N < Br < I ~ S ~ C and with the similar nephelauxetic series[24], in which the ligands are arranged according to decreasing Racah parameters (decreasing interelectronic repulsion). In fact a correlation between the IS and the nephelauxetic series of the ligands has been observed in Fe(II) high-spin complexes[1]. By contrast, the IS in the presumably more covalent Fe(II) low-spin complexes correlates with the spectrochemical series of the ligands[13]. Preliminary measurements for Ir(III) (low-spin) complexes are likewise indicating a correlation between the IS and the spectrochemical series of the ligands[12].

Within the framework of our LCAO-MO model, π-donor properties of the ligands should not affect the total electron density at the nucleus in both Au(I) and Au(III) compounds. This is a consequence of the compensation of the charge transfer in bonding and accociated antibonding d_π-MOs, which are fully occupied. The IS in the studied gold compounds is thus a mere function of the σ-donor and π-acceptor properties of the ligands.

Au(III) compounds: In the absence of π-acceptor bonding the IS in trivalent gold complexes depends on the atomic populations of the σ-bonding b_{1g}- and a_{1g}-MOs at the gold ion. The $6s(a_{1g})$- population contributes positively to the total electron density at the nucleus, while the d-parts diminish it by shielding effects. Since a monotonic correlation between the IS and the spectrochemical series is experimentally observed, and since the σ-donor

strength of ligands increases with their rank in the spectrochemical series, we

conclude that the IS increases with covalency in the σ-bonds. This is also

supported by the results of MO calculations[52,53]: the electronic configuration

of the Pt(II) ion in the square-planar $PtCl_4^{2-}$, $Pt(+0.24)5d^{8.61}6s^{0.66}6p^{0.49}$,

shows a substantial 6s-population at the metal, and the metal 6s-electrons

participate strongly in the bonding with the ligands. Thus the IS in gold

compounds with monoatomic ligands increases with the σ-donor strength. In

these cases the bonding should not have any π-acceptor component, since ligand

valence shell expansion is unlikely to occur in oxidation states higher than

$+2$[54].

The increase in the IS with increasing size of the cations, as observed

for gold tetrachlorides and oxides, can be explained by an increase in σ-

covalency with decreasing interatomic distance, if it is assumed that the

length of the Au-ligand bond is reciprocally related to the size of the cations.

This assumption is based on the ligand field splitting in Co-halide complexes,

which increases with the size of the cations as well as with pressure[37]. The

IS of the Au(III) oxides reveales a stronger dependence on the size of the

cations than that of the chlorides. This indicates a significantly larger

change in covalency, if the bond length is shorter.

Ligands like CN^-, which have their own π-system, may accept electron

density from d_π-MOs by back bonding if the empty π^*-ligand orbitals are

sufficiently stable. This back donation causes a decrease in the shielding of

s-electrons by the atomic 5d-populations on the gold ion and due to synergic

coupling an increase in the σ-donor strength, resulting in a larger $e|\psi(o)|^2$.

In Au(III) cyanide complexes π-acceptor bonding can presumably be neglected

against a strong σ-donor component[54], since the levels of the Au(III) ion are relatively stable. This conclusion is in agreement with an analysis of the band intensities in $KAu(CN)_4$, which reveals only weak π-bonding[55]. The large IS in the Au(III) tetracyanides is therefore mainly caused by the high σ-donor capacity of the CN^- ligand, a fact which has plenty of experimental evidence[56].

Electronic spectra of $Au(N_3)_4^-$ and $Au(SCN)_4^-$ in the optical and and near UV region show a high covalency of the Au-ligand bond and evidence for a weak π-donor bond[29,36]. A decreasing π-donor strength from Cl^- to N_3^- and further to S-bound SCN^- [57] as well as a weak π-acceptor component in the tetracyanide are in good agreement with the positions of the compounds in the IS scale (Fig. 3).

From valence force constants was concluded, that the Au-CN bond is nearly the same in $KAu(CN)_2Br_2$ as in $KAu(CN)_4$, and that the Au-ligand bonds have strongly directional character[58]. This agrees well with our finding of the IS of $KAu(CN)_2Br_2$ to be the arithmetic mean of the IS values of the tetracyanide and the tetrabromide.

Au(I) compounds: Again a higher σ-donor strength of the ligands causes a higher atomic population of the bonding a_{1g}-MO at the gold ion. The atomic 6s-population of this MO at the gold ion increases at the same time, with the antibonding $a_{1g}(\sigma^*)[5d_{z^2}]$ - MO being destabilized. The atomic population of the antibonding $e_{1g}(\pi^*)[5d_{xz,yz}]$ - MO on the gold as well as the shielding of s-electrons from the nucleus decrease with increasing π-acceptor strength of the ligands. The IS therefore increases with increasing σ-donor and π-acceptor strength of the ligands, as in the case of Au(III), with the π-donor properties not directly affecting the IS.

When compared with the spectrochemical series, the positions of AuI and AuCl in the IS scale are reversed. This may be due to a shift in the levels of the iodide ligand, which was suggested to explain the extremely high energy for complex formation of B-type $5d^{10}$- iodides, especially of AuI [54]. In this way, backbonding from d_π-MOs to empty halide orbitals becomes possible, thus augmenting the electron density at the nucleus.

The 5d-orbitals of Au(I) are less stable than those of Au(III). Therefore one may expect a considerable π-acceptor component in the Au(I)-cyanides [54]. Jones [55] deduced from Au-C and C-N force constants that π-bonding is stronger in $KAu(CN)_2$ than it is in $KAu(CN)_4$, which may explain the smaller difference of ISs between $KAu(CN)_4$ and $KAu(CN)_2$ than between $KAuCl_4$ and AuCl.

In the Dewar-Chatt-Duncanson model, the bonding of olefin ligands with transition metal ions is described by a donation of π-electrons of the C-C bond to σ-type metal orbitals and a synergic π-backbonding to empty antibonding orbitals of the olefin ligands [59], in obvious similarity to the bonding in the cyanide complexes. Accordingly, the IS of the olefin-AuCl complexes is significantly larger than in AuCl.

c) Correlation between QS and IS.

The electric field gradient (EFG) at the nucleus is given by

$$q = q_{vaL}(1 - R) + q_{lat}(1 - \gamma_\infty)$$

where q_{vaL} denotes the direct contribution of the valence electrons and q_{lat} the direct contribution of the lattice. The atomic and lattice Sternheimer factors are given by $(1 - R)$ and $(1 - \gamma_\infty)$, respectively, with no theoretical

calculations being available for the Au atom at the present time. For Bi^{3+} a value for $\gamma_\infty = -42.4$ was nonrelationistically calculated[60] (which therefore might be too large). Because of the r^{-3}-dependence of the EFG the lattice contribution may be neglected in strongly covalent compounds, except for very high lattice Sternheimer factors. If q_{lat} is estimated in a point charge model and γ_∞ is approximated by the theoretical Bi^{3+}-value, one obtains a lattice contribution of about 10% of the total EFG in Au complexes. Therefore the lattice contribution to the EFG will be neglected in the following discussion.

The contribution of the valence electrons to the EFG can be estimated from atomic field gradients[61,62]. From the magnetic hyperfine structure of the metastable $5d^9 6s^2\ ^2D$ state of the gold atom a value $\langle r^{-3} \rangle_{5d} = 12.3\ a_o^{-3}$ was determined for the 5d-electrons. For 6p-electrons of Au no direct experimental determination of $\langle r^{-3} \rangle$ is known. A value of $\langle r^{-3} \rangle_{6p_{3/2}} = 16.4\ a_o^{-3}$ was deduced by Machmer[65], using the magnetic HFS-constant of the $6p_{1/2}$-electrons[63] and the ratio of the magnetic HFS-constants of $6p_{3/2}-$ and $6p_{1/2}-$ electrons[64] of ^{197}Au.

The atomic contribution to the EFG in strongly covalent Au-compound is mainly a function of the atomic 6p- and 5d- populations of the MOs at the gold ion and therefore of the donor and acceptor properties of the ligands. As pointed out below, the absolute value of the EFG in Au complexes is monotonically increasing with the σ-donor and π-acceptor properties of the ligands, as is the total electron density at the nucleus. The experimentally observed correlation between QS and IS is therefore qualitatively understood as a consequence of the high covalency of the Au-ligand bonding. The approximate linearity of the

QS-IS correlation, however, as it was established in this work and by Ref.[16],

requires that the ratios of s- and d- charge transfer are approximately

constant for the various complexes studied. Similarly, a linear correlation

between QS and IS was also reported for low-spin Fe(II) complexes[13].

<u>Au(III) compounds</u>: MO-calculations for the $AuCl_4^-$-complex[52] showed that the

empty antibonding $b_{1g}(\sigma^*)[5d_{x^2-y^2}]$ - MO has 90% metal character. This

$5d_{x^2-y^2}$ -hole in the 5d-shell of Au produces a negative EFG, which is partly

compensated by the positive contribution of the atomic population of the

bonding b_{1g}-MO. The contributions of the various atomic 6p-populations have

opposite signs: the σ-bonding e_u-MOs contribute positively, the π-bonding

a_{2u}-MOs negatively to the total EFG. Since the overlap of the σ-bonding

orbitals is usually considerably larger than that of the π-bonding orbitals,

the contribution of the 6p-populations to the EFG will mainly be determined by

the $6p_{x,y}$-populations of the $e_u(\sigma)$ - MO, being therefore positive. Since the

experimental $\langle r^{-3} \rangle$ -value of 6p-electrons is larger than that of 5d-electrons,

a small and presumably positive total EFG is therefore expected for $AuCl_4^-$,

in agreement with the small QS observed for the tetrachlorides.

    With increasing σ-donor strength of the ligands, the atomic populations

of the σ-bonding b_{1g}- and $e_u(\sigma)$ - MOs at the gold ion are augmented. In this

way, the EFG, which we assume to be positive, is enlarged with the 5d-hole

being more and more filled and with the positively contributing 6p-populations

of the $e_u(\sigma)$ - MO increasing. In those Au complexes where an intra-ligand

π-system exists, π-backbonding to empty π^*-ligand orbitals reduces the atomic

populations of the $b_{2g}(\pi^*)[5d_{xy}]$- and the $e_g(\pi^*)[5d_{xz,yz}]$ - MOs at the Au ion.

Since the first MO has a higher energy and the second one a higher total

population, one may assume that the amount of back-donated electron charge is comparable in both symmetry groups. Since both MOs contribute with opposite sign to the EFG, no direct effect on the EFG is therefore expected. A synergic coupling of the σ- and π- bonds, however, gives a positive contribution to the EFG, therefore increasing the QS with increasing π-acceptor strength of the ligands.

Au(I) compounds: σ-donor bonding affects the atomic populations of the $a_{2u}[6p_z]$- and $a_{1g}[5d_{z^2}]$- MOs at the gold ion, which give both negative contributions to the EFG. The EFG, presumably being negative, is therefore increasing with increasing σ-donor strength of the ligands. A synergic decrease in the population of the π-bonding $e_{1u}[6p_{x,y}]$- MO, caused by increasing σ-donor strength of the ligands, additionally augments the EFG by reducing the positive contributions of the $6p_{x,y}$-electrons. d_π-backbonding lowers the atomic populations of the $e_{1g}(\pi^*)[5d_{xz,yz}]$- MOs at the gold ion, resulting in a positive direct contribution to the EFG. Because of synergically increasing covalency in the σ-bonds, especially in the $6p_\sigma$-bonds, the direct contribution is probably overcompensated by the corresponding negative contribution of the σ-populations.

According to our discussion, the QS in Au(I) and Au(III) complexes will increase with increasing σ-donor and π-acceptor strengths of the ligands, in agreement with the experimental result. For a test of the relevance of our interpretation of QS and its correlation with IS, an experimental determination of the sign of the EFG in Au(I) and especially Au(III) compounds is highly desirable.

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Table 1. Compilation of results obtained for Au(I) and Au(III) compounds at 4.2 K: Isomer shift IS relative to ^{197}Pt$\underline{Pt}$-source, electric quadrupole splitting $QS = (eQ_g V_{zz}/2)(1 + \eta^2/3)^{1/2}$, experimental linewidth W and absorber thickness d. In the last column references to the suppliers or the preparation of the samples are given.

Compound	IS [mm/sec]	QS [mm/sec]	W/2 [mm/sec]	d [mg/cm^2 of Au]	Ref.
Au(III) compounds					
CsAuF$_4$	+0,09±0,02	0,75±0,04	0,99±0,02	50	a
RbAuF$_4$	+0,05±0,02	0,17±0,35	1,05±0,05	50	a
As(C$_6$H$_5$)$_4$Au(Az)$_4$*	+0,19±0,02		0,90±0,03	46	g
KAuJ$_4$	+0,43±0,05	1,28±0,10	0,96±0,06	110	e
AuBr$_3$	+0,48±0,07		0,94±0,03	80	b
KAuBr$_4$	+0,60±0,03	1,13±0,06	0,89±0,04	72	b
HAuCl$_4$ · 4H$_2$O	+0,66±0,04	0,94±0,08	0,85±0,07	125	b
NaAuCl$_4$ · 2H$_2$O	+0,81±0,05	1,21±0,10	0,90±0,08	120	b
KAuCl$_4$	+0,81±0,03	1,11±0,06	0,88±0,03	140	b
NH$_4$AuCl$_4$	+0,87±0,03	1,18±0,06	1,03±0,03	102	c
(C$_4$H$_9$)$_4$NAuCl$_4$	+1,02±0,06	1,31±0,14	1,10±0,10	100	d
C$_{12}$H$_{10}$N$_2$AuCl$_3$	+1,32±0,03	1,94±0,06	0,95±0,04	170	h
KAu(SCN)$_4$	+1,63±0,07	2,04±0,14	1,06±0,08	78	f
As(C$_6$H$_5$)$_4$Au(N$_3$)$_4$	+1,66±0,05	2,89±0,10	0,98±0,04	80	g
Au$_2$O$_3$ · H$_2$O	+1,31±0,08	1,69±0,16	1,11±0,16	170	b

(continued)

Table 1. (continued)

Compound	IS [mm/sec]	QS [mm/sec]	W/2 [mm/sec]	d [mg/cm^2 of Au]	Ref.
		Au(III) compounds			
Li_3AuO_3	+1,95±0,04	2,27±0,08	1,00±0,04	112	j
Na_3AuO_3	+2,45±0,04	3,02±0,08	1,07±0,06	145	j
$AuO(OH)$	+1,38±0,03	1,71±0,06	1,10±0,03	120	e
$KAu(CN)_2Br_2$	+2,65±0,04	5,34±0,08	0,95±0,02	105	i
$KAu(CN)_4$	+4,03±0,06	6,86±0,12	0,98±0,03	92	i
		Au(I) compounds			
$AuCl$	-1,37±0,02	4,47±0,04	0,91±0,02	285	f
AuJ	-1,21±0,04	3,91±0,08	0,91±0,04	210	f
$As(C_6H_5)_4Au(Az)_2$*	-1,06±0,03		0,84±0,03	56	g
$C_{10}H_{12} - AuCl$	+0,83±0,02	6,04±0,04	0,96±0,03	120	k
$C_{18}H_{36} - AuCl$	+0,91±0,03	6,41±0,06	1,06±0,05	185	k
$C_{16}H_{32} - AuCl$	+1,03±0,03	6,29±0,06	0,99±0,04	96	k
$As(C_6H_5)_4Au(N_3)_2$	+1,43±0,05	6,84±0,10	0,92±0,05	74	g
$AuCN$	+2,30±0,04	8,00±0,08	0,90±0,04	125	c, b
$KAu(CN)_2$	+3,12±0,09	10,12±0,18	0,87±0,06	140	b

Table 1. (continued)

*
<u>Az</u> stands for the Ligand — C

C_6H_{11}

(tetrazole ring structure with nitrogen atoms)
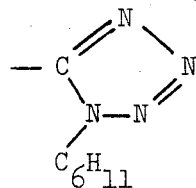
[a]Prof. Hoppe, Univ. Giessen, Germany

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[j]Dr. Wasel-Nielen, Univ. Giessen, Germany

[k]Prof. Hüttel and Dr. Konietzny, Univ. München, Germany

Figure Captions

Fig. 1. Absorption spectra of the 77 keV γ rays measured for various Au(III)

compounds. The solid curves represent the result of least square fits.

The positions of the individual lines are indicated by dashed lines.

Fig. 2. Absorption spectra of the 77 keV γ rays measured for various Au(I)

compounds. The solid curves represent the results of least squares fits.

The positions of the individual lines are indicated by dashed lines.

Fig. 3. Graphical representation of the isomer shift IS obtained for various

Au(I) and Au(III) compounds at 4.2 K, with respect to the ^{197}PtPt-source.

Fig. 4. Electric quadrupole splittings QS versus isomer shift IS for various

Au(I) and Au(III) compounds at 4.2 K.
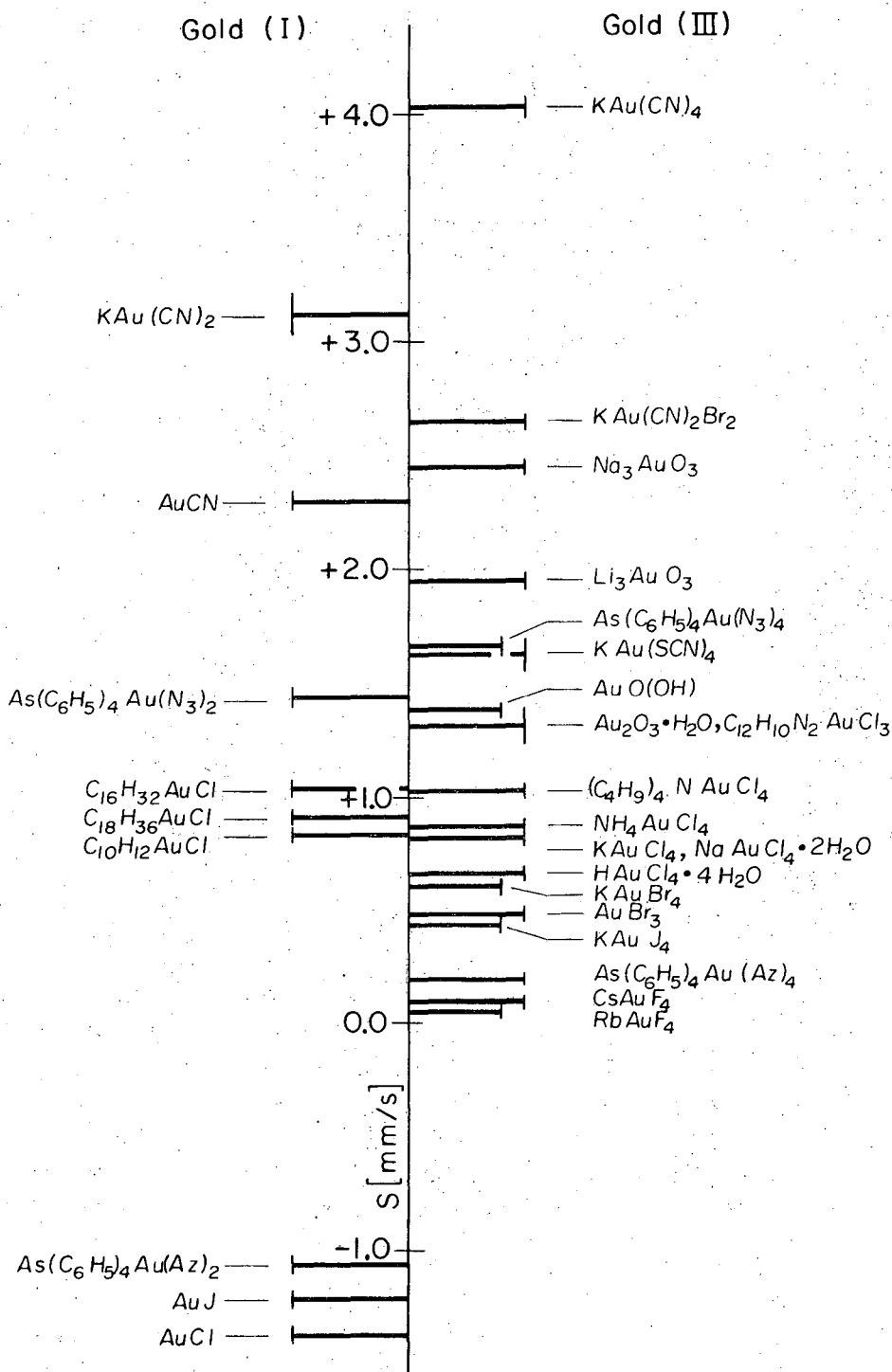
Fig. 3

XBL707-3313

Fig. 4

XBL707-3314