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MÖSSBAUER ISOMER SHIFTS IN CHEMICAL SYSTEMS OF GOLD

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1. Introduction

The 77.3-keV gamma transition in monoisotopic ^{197}Au is well suited for chemical applications of Mössbauer spectroscopy, since the observed ranges of both isomer shifts and electric quadrupole splittings cover several experimental linewidths. Isomer shift measurements with chemical compounds of gold, especially monovalent and trivalent halide complexes, were first reported by ROBERTS et al. [1962] and by SHIRLEY et al. [1964a]. It was not until 1970, however, that further applications of this gamma resonance to chemical problems were reported, when different groups published their results of systematic Mössbauer studies of various inorganic Au(I) and Au(III) compounds (FALTENS [1969]; FALTENS and SHIRLEY [1970]; CHARLTON and NICHOLS [1970]; BARTUNIK et al. [1970a]). Quite recently, this work has been extended to inorganic Au(V) compounds (KAINDL et al. [1973]) and to gold compounds with organic ligands (JARVIS et al. [1973]; BARTUNIK [1974]).

The results of these studies as a whole reveal a dependence of the isomer shift on the formal oxidation state similar to the one found in compounds of the 3d, 4d, and 5d transition elements, e.g., ^{57}Fe, ^{99}Ru, ^{193}Ir, and ^{189}Os (see chs. 7 and 8a). Furthermore, appreciable variations of the isomer shifts within the same oxidation state were observed for aurous and auric compounds, much as in the cases of Ru(II) and Ru(III) (KAINDL et al. [1969]; POTZEL et al. [1970]); Ir(III) (WAGNER and ZAHN [1970]); and Fe(II) low-spin complexes (BANCROFT et al. [1970]). These variations indicate a marked dependence of the isomer shift on the nature of the ligands. Gold compounds have turned out to be particularly suitable for a study of the correlation between the isomer shifts and the chemical properties of the ligands, since gold—within the same oxidation state—forms many highly covalent "model" compounds of the same molecular symmetry and with simple ligands.

2. Properties of the 77.3-keV Gamma Resonance

The decay scheme of 18-h ^{197}Pt, which usually serves as the source activity for ^{197}Au Mössbauer experiments, is shown in fig. 8b.1. Strong single-line sources of ^{197}Pt are easily obtained by neutron irradiation of natural platinum metal or, preferably, of highly enriched ^{196}Pt metal. The neutron-activated platinum foils may be used as Mössbauer sources without further treatment. Since the resonance fractions for most compounds are sufficiently large at 4.2 K and rather high counting rates of the 77.3-keV gamma rays are obtainable (with either NaI(Tℓ) or Ge(Li) detectors), Mössbauer transmission experiments with the ^{197}Au gamma resonance usually consume little time and are fairly simple; in this respect they are comparable to the ^{57}Fe case.

The resolution provided by the 77.3-keV resonance for chemical applications is nearly equal to that of the ^{57}Fe gamma resonance, despite the much larger natural linewidth. Both isomer shifts and electric-quadrupole coupling constants are, due to the magnitudes of the relevant nuclear parameters of both nuclear states and the high atomic number of gold, much larger in the ^{197}Au case than in the ^{57}Fe case; the drawback of a wider absorption line is thus almost completely compensated. The halflife of the $1/2^+$ excited state of ^{197}Au at 77.3 keV has recently been remeasured as $T_{1/2} = 1.93 \pm 0.03$ ns (LYNCH [1973]), which corresponds to a minimum experimental linewidth of the resonance line of $W_0 = 1.87 \pm 0.03$ mm/s. A previously reported anomalous narrowing of the absorption line in AuCN and $KAu(CN)_2$ by about 13% relative to the natural linewidth (POTZEL and PERLOW [1972]) has not been confirmed by the subsequent results of other workers (PFEIFFER et al. [1973]; BARTUNIK and KAINDL [1973]); instead, it was found that the experimental linewidths observed for both compounds with a platinum metal source after extrapolation to zero absorber thickness agree very well with the natural linewidth resulting from the electronically measured half-life of the 77.3 keV state.

No magnetic hyperfine interactions have been observed in the studied gold compounds with oxidation states I, III, and V, in agreement with their diamagnetic properties. Therefore, only lineshifts or electric-quadrupole splittings are observed in the absorption spectra. In the presence of an electric field gradient (EFG) at the gold nucleus, the $1/2^+ \rightarrow 3/2^+$ transition splits into a doublet separated by

$$\Delta E_Q = 1/2\ e^2\ Q\ q_{zz}\ (1 + 1/3\ \eta^2)^{1/2}$$

where $Q = +0.594 \pm 0.010$ b (BLACHMANN et al.[1967]) is the electric quadrupole moment of the nuclear ground state and where q_{zz} and the asymmetry parameter η describe the EFG tensor in the usual notation.

In many cases the observed quadrupole doublet is found to be rather asymmetric. This may be due to either a texture of the absorber or a strongly anisotropic Mössbauer resonance factor, causing the Goldanskii-Karyagin effect (KARYAGIN [1966]). Indeed, taking into account the recently determined value for the E2/M1-mixing ratio δ of the 77.3-keV gamma transition, $\delta(E2/M1) = -0.353 \pm 0.007$ (WORTMANN et al. [1973]), the intensity ratio of the two quadrupole-split lines may vary between the extremes of 0.74 and 1.16 as a function of the angle between the direction of observation and the axis of an axially symmetric EFG. This property has recently been exploited in determining the sign of the EFG in $KAu(CN)_2$ using a single-crystal absorber (PROSSER [1973]). Appreciable line asymmetries due to the Goldanskii-Karyagin effect have to be expected in many cases, since gold compounds -due to their molecular structure- should often display rather anisotropic Mössbauer resonance factors. If a quadrupole-split doublet of unequal line intensities is observed for a texture-free polycrystalline absorber, information can be gained on the anisotropy of the Mössbauer resonance factor and hence on the tensor describing the mean-square displacement of the absorbing atoms.

The change in the mean-square nuclear charge radius, $\Delta \langle r^2 \rangle$, has been estimated by several authors (ROBERTS et al.[1969]; SHIRLEY [1964b]; FALTENS and SHIRLEY [1970]; KAINDL et al. [1973]). Despite the controversy about its absolute magnitude, a positive sign

has been assumed in all cases; this means that the isomer shift increases with increasing electron density, $\rho(0)$, at the nucleus.

3. Inorganic Compounds

By far the majority of gold compounds is monovalent or trivalent; it was only very recently that a few extremely reactive pentavalent gold-fluoride complexes were synthesized (LEARY and BARTLETT [1972]), which were subsequently studied by gamma resonance spectroscopy (KAINDL et al. [1973]).

A compilation of the data for the isomer shifts S and the electric-quadrupole splittings ΔE_Q of all inorganic gold compounds studied so far is given in table 8b.1. Several compounds have been studied by different groups, and the results usually agree within the limits of error. In these cases an adopted value is presented. If a published result has not been used for forming the adopted value, the reference for the respective publication is set in parentheses. In a few cases, where large discrepancies could not be resolved on the basis of the existing data, all such data have been included in the table and identified by an asterix. Such discrepancies may, for example, be due to the chemical instability of a compound. An inspection of table 8b.1 clearly shows that the isomer shifts of gold compounds depend on both the formal oxidation state of the metal ion and on the chemical nature of the ligands. The characteristic features of this relationship will be discussed in the following paragraph on the basis of a simple LCAO model.

For a given ligand, the isomer shift increases with increasing formal oxidation state of gold (§ 3.1). Superimposed, however, is a

strong dependence of S on the nature of the ligands (§ 3.2), which is interpreted in terms of a correlation between S and the parameter of the spectrochemical series of ligands. Both for aurous and auric compounds an approximate linear relationship between S and ΔE_Q is observed (§ 3.3). The results of high-pressure experiments with aurous and auric compounds, which represent a test for the correctness of the model, will finally be discussed in § 3.4.

3.1. Isomer Shift and Oxidation State

In fig. 8b.2 the isomer shift data of table 8b.1 are displayed in three distinct groups according to the formal oxidation state of gold. In addition, data for gold-organic compounds (see table 8b.3) are included. From an inspection of fig. 8b.2, it becomes quite obvious that the formal oxidation state is not the dominant parameter in determining the isomer shift. This is not surprising for the highly covalent gold complexes, since there is plenty of evidence that the electroneutrality principle (PAULING [1963]) holds in covalent compounds and leads to both rather small total charges on the atoms and relatively little variations in these charges with the formal oxidation state. The ranges of isomer shifts for aurous and auric compounds overlap completely, demonstrating a strong dependence of the isomer shift on the nature of the ligands. A behaviour like this is not unique to gold compounds, and has also been observed for inorganic complexes of other d-transition elements like iron (BANCROFT et al.[1970]), ruthenium (KAINDL et al. [1969]; POTZEL et al. [1970]), and iridium (WAGNER and ZAHN [1970]).

Nevertheless, a typical increase of the total electron density at the nucleus, $\rho(0)$, with increasing oxidation state is usually observed for d-transition metal complexes with "innocent" ligands, like F^-, $C\ell^-$, Br^-, I^-, O^{2-}, and NH_3; this is interpreted as resulting from a decrease in the shielding of s-electrons with a decreasing number of d-electrons. Figure 8b.3 clearly shows this behaviour for the gold compounds, especially if one compares compounds with the same ligands but with different oxidation states. A quantitative description, however, of the observed increase in $\rho(0)$ in the series Au(I) < Au(III) < Au(V) in terms of a decrease in the 5d occupation of gold (accompanying the increase in the formal oxidation state) cannot easily be given since the gold coordination varies considerably with the oxidation state: monovalent gold complexes usually contain linear ligand-gold-ligand units with $D_{\infty h}$ symmetry in the first coordination sphere, while most of the trivalent gold complexes have a square-planar molecular structure with D_{4h} symmetry; the pentavalent complexes have octahedral molecular symmetry (O_h) (LEARY et al. [1973]). The example of AuF_3, where the trivalent gold ion is surrounded by six F^- ligands forming a distorted octahedron (EINSTEIN et al. [1967]) shows that a difference in the coordination number can considerably affect the isomer shift. In addition, the dependence of bond covalencies on the oxidation state has to be taken into account, if isomer shifts in compounds with identical ligands but different oxidation states of gold are discussed. Therefore, a characterization of the oxidation state of gold from isomer shifts alone is not generally feasible.

3.2. Isomer Shift and Nature of Ligands

A dependence of the total electron density at the nucleus on the nature of chemical bonding, as it is observed for compounds of gold, can be understood qualitatively in a simple LCAO-MO model. Positive contributions to $\rho(0)$ arise from the atomic 6s-populations of the molecular orbitals on the gold ion. On the other hand, a decrease of $\rho(0)$ is caused by the atomic 5d-populations of the MOs, due to their shielding effect. The atomic 6p-populations yield only small contributions both by their shielding of s-electrons and by their relativistic density at the nucleus (see ch. 2). The relative magnitudes of these various contributions are well known from the study of optical isotope shifts (KOPFERMANN [1956]) and from the results of Dirac-Fock calculations for free gold ions with different electronic configurations (MANN[1968]). While the negative (shielding) contribution of one 5d electron to $\rho(0)$ is considerable, viz. of the order of 20% of the positive contribution of one 6s electron, the small positive and negative contributions of 6p electrons to $\rho(0)$ almost cancel each other. Hence, the isomer shift is expected to depend mainly on the atomic 6s- and 5d-populations. For highly covalent complexes like the gold compounds, these populations depend on the number and the kind of ligands attached to the central metal ion.

A quantitative interpretation of isomer shifts in highly covalent transition metal complexes would require molecular-orbital calculations of the self-consistent field type. Since such calculations are not yet available, phenomenological ligand parameters like the electronegativity (FALTENS and SHIRLEY [1970]) or the spectrochemical

character (CHARLTON and NICHOLS [1970]; BARTUNIK et al. [1970a]) have been used to interprete the dependence of the isomer shift on the ligands.

For trivalent gold compounds the isomer shift has been found to increase along the series of ligands

$$F^- < I^- < Br^- < Cl^- < SCN^- \sim N_3^- < O^{2-} \ll CN^- .$$

This hardly agrees with any scale of ligand electronegativities. With the only exception of the fluorine ligand, however, it is in good agreement with the spectrochemical series, where the ligands are arranged according to the frequency of the optical transitions between the highest antibonding d-molecular orbitals of the transition metal complex (JØRGENSEN[1962]). For Au(III) complexes this transition occurs between the $b_{1g}(\sigma^*)$ - $5d_{x^2-y^2}$ and the $b_{2g}(\pi^*)$ - $5d_{xy}$ molecular orbitals. For Au(I) complexes, which exhibit quite similar a correlation between the isomer shifts and the spectrochemical ordering of the ligands, the corresponding transition occurs between the $a_{1g}(\sigma^*)$ - $5d_{z^2}$ and the $e_{1g}(\pi^*)$ - $5d_{xz,yz}$ molecular orbitals.

The results of optical experiments under high pressure and of the study of Racah parameters have shown that a relationship exists between the magnitude of these transition frequencies and the electron densities in the outer shell. The variation of the ligand-field splitting, Δ, has been interpreted in terms of σ and π electron donor and acceptor properties of the ligands (JØRGENSEN [1962]). For octahedral and square-planar complexes, Δ is given by the relation

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

The first term describes the crystalline-electric field and can be neglected for highly covalent complexes. The other terms originate from covalency effects in σ- and π-bonding molecular orbitals; the direction of electronic charge transfer is indicated by the arrows in the parentheses.

On this empirical basis, the behaviour of isomer shifts within a given oxidation state of gold, especially the correlation with the spectrochemical series of ligands, can be understood qualitatively, since the electron density at the gold nucleus, $\rho(0)$, depends strongly on the donor and acceptor properties of the ligands. Thus, a partial delocalization of electron density in σ-bonding orbitals from σ-donating ligands to the metal will lead to a net increase in $\rho(0)$ due to the direct 6s contribution. A delocalization of electrons in antibonding π-MO's from the metal to π-accepting ligands will also cause $\rho(0)$ to increase, since the 5d population on the gold ion is decreased. Hence, $\rho(0)$ and Δ are expected to be smaller for the σ-accepting and π-donating halide ligands than for the σ-donating and π-accepting (back-bonding) cyanide ligands.

The electroneutrality principle (see ch. 3.1) suggests a synergic coupling between the σ-donor and π-acceptor strengths of a ligand. Therefore, transfer of electronic charge in a σ-bond should be greatly compensated by a transfer with opposite direction in a π-bond (GRAHAM [1968]). The relationship between isomer shifts and quadrupole splittings in gold compounds (see next section) is found to be consistent with this concept(CHARLTON and NICHOLS [1970]; BARTUNIK et al. [1970a]).

Although, the qualitative agreement between an arrangement of ligands according to the isomer shifts of gold compounds and the spectrochemical series should not be stressed too heavily, one may point out some finer details of agreement. The isomer shifts in the tetrachlorides increase with increasing size of the cations. This behaviour parallels the increase of the ligand field splitting with the size of cations, which was observed for halide complexes of Co (COTTON et al.[1961]) and Ni (ASMUSSEN and BOSTRUP [1957]). The isomer shifts of a few aurous and auric compounds with mixed ligands (like $KAu(CN)_2Br_2$, for example) are found to be very close to the arithmetic means of the isomer shifts of the respective compounds with single ligands (like $KAu(CN)_4$ and $KAuBr_4$). This is equivalent to Tsuchida's average environment rule (JØRGENSEN[1962]), which often allows one to predict the ligand-field splitting of an octahedral complex with mixed ligands $ML_1L_2 \cdot \cdot L_6$ from the ligand-field splitting of the complexes $M(L_i)_6$ with the single ligands L_i. In fact, this introduces the concept of partial isomer shifts, which has already been used in an analysis of isomer-shift results for Fe(II) low-spin complexes (BANCROFT et al. [1970]). The worth of such a quantitative classification of ligands is questionable, since one expects saturation effects in, e.g., the delocalization of electron density from the metal to the ligands, when the number of electron-accepting ligands increases. This should lead to a variation of partial isomer shifts with the relative number of such ligands for a given coordination number; an effect like this has been discussed in the case of ruthenium compounds (POTZEL et al.[1970]).

A correlation between the isomer shift and the spectrochemical series of ligands has also been observed for Os, Ir, Pt, and Ru compounds (ch. 8a). In all these cases, the isomer shifts for compounds with fluorine ligands do not fit well into this correlation (BANCROFT et al. [1970]). This may arise from a relatively higher total electronic charge on the fluorine ligands. In this case, the ligand-field splitting can be relatively large, since the crystal field contribution may no longer be negligible.

3.3. Correlation between Isomer Shift and Electric-Quadrupole Splitting

With a few exceptions only, for both aurous and auric compounds an approximately linear correlation between isomer shifts and quadrupole splittings has been observed. This is demonstrated in figs. 8b.4 and 8b.5, where ΔE_Q is plotted versus S for various aurous and auric compounds, respectively. Furthermore, the monovalent compounds have in most cases larger ΔE_Q values than the trivalent compounds with the same ligands. Thus, it will often be possible to determine the formal oxidation state of gold in a compound from a knowledge of both the isomer shift and the electric-quadrupole interaction. Before discussing the correlation between S and ΔE_Q, a few comments on the origin of quadrupole interaction in gold compounds are necessary.

The total electric-field gradient at the nucleus can be written as

$$q = q_{val}(1 - R) + q_{\ell at}(1 - \gamma_\infty)$$

where q_{val} is the contribution of the valence electrons and $q_{\ell at}$ describes the lattice contribution; R and γ_∞ are the inner and outer

Sternheimer factors, respectively. For highly covalent compounds the main contribution to q is expected to stem from the valence electrons. Since S is also determined by the valence electrons, a correlation of the isomer shift with ΔE_Q can be expected on the basis of a single LCAO-MO model.

The individual contributions of the valence electrons to the electric-field gradient can be estimated from atomic electric-field gradients and the theory of DAILY and TOWNES [1955]. For p and d orbitals the atomic electric-field gradients are given in tables 8b. 2. Taking into account experimental and theoretical $\langle r^{-3} \rangle$ values for gold, one expects that both 6p and 5d orbitals substantially contribute to q_{val}. For 5d electrons, an $\langle r^{-3} \rangle$ value of 12.3 a_o^{-3} was determined by CHILDS and GOODMANN [1966], while MACHMER [1966] estimated an $\langle r^{-3} \rangle$ value of 14.6 a_o^{-3} for 6p electrons.

A qualitative interpretation of the ΔE_Q - S correlation is especially straightforward in the case of Au(I) compounds. Here σ bonds can be formed with the $5d_{z^2}$ and 6s metal orbitals of a_{1g} symmetry, and with the $6p_z(a_{2u})$ orbitals, while π-bonding involves the $5d_{xz,yz}(e_{1g})$ and $6p_{x,y}(e_{1u})$ orbitals. Both the $5d_{z^2}$ and $6p_z$ orbitals cause negative contributions to the electric-field gradient (table 8b.2). With an increasing σ-donor strength of the ligands the absolute value of the electric-field gradient is expected to increase, if its sign is assumed to be negative for aurous compounds. A contribution of negative sign is also produced by a synergic decrease in the population of π-bonding $6p_{x,y}$-MO's. The postulation of a negative electric-field gradient has recently been confirmed for $KAu(CN)_2$, where a negative sign was derived

from a study of line intensities using a single-crystal absorber (PROSSER[1973]).

Back bonding of d_π electrons primarily lowers the atomic population of the $5d_{xz,yz}$-MO's on the gold ion, causing a positive contribution to the electric-field gradient. Because of the synergically increased transfer of charge from the ligands to the metal in the σ-bonds, especially in the $6p_z$-bonds, the direct contribution can be overcompensated by the corresponding negative σ-contribution.

In auric compounds the situation is not as simple, since the total electric-field gradient is composed of contributions with different signs. The main contributions are given by the σ-bonding $5d_{x^2-y^2}$ and $6p_{x,y}$ orbitals (positive), and by the $5d_{x^2-y^2}$ hole in the gold 5d shell (negative). Since the experimental $\langle r^{-3} \rangle$ values are larger for the 6p than for the 5d electrons, relatively small and presumably positive electric-field gradients are expected for auric compounds. Even though no sign has yet been determined for the electric-field gradient in any of the auric compounds, rather small values of ΔE_Q have been measured in auric halides, in agreement with the above description.

With increasing σ-donor properties of the ligands, the atomic populations of the σ-bonding $5d_{x^2-y^2}$ and $6p_{x,y}$ MO's on the trivalent gold ion will become larger, causing positive contributions to the electric-field gradient. A synergic weakening of the π-bonds will not lead to a further important contribution, since the positive contribution of the $5d_{x,y}$ electrons to the electric-field gradient and the negative contribution of the $6p_z$ electrons tend to compensate one another. Since π-acceptor bonding is expected to play a less-important

role for auric cyanides, thiocyanides, and nitrosyl complexes (JØRGENSEN [1962]; JONES and SMITH [1964]) we will not discuss its influence on the ΔE_Q - S correlation (see BARTUNIK et al. [1970a]). FALTENS and SHIRLEY [1970] have based their interpretation of the correlation between S and ΔE_Q on the assumption of sp-hybrid bonding in the monovalent and of dsp^2-hybrid bonding in the trivalent gold compounds. With this model, the approximately linear relationship between S and ΔE_Q can also be explained and the same predictions for the signs of the electric-field gradient have been made as in the above discussion. Such a hybrid models, however, completely neglects the rather important effects of π bonding, and is therefore not quite appropriate for quantitative evaluations.

3.4. Effects of High Pressure

A study of the influence of high pressure on the hyperfine interaction parameters of gold compounds is quite useful as a test for the above interpretations. Due to the high gamma ray energy, the 100% abundance of the ^{197}Au isotope, and the relatively good resolution obtainable with the 77.3-keV gamma resonance such experiments are rather straightforward. Experimental details on high-pressure Mössbauer work are given in ch. 6b.

The first high-pressure Mössbauer study of chemical compounds of gold was made on the trivalent compounds $KAuCl_4$ and $KAu(CN)_4$ (BARTUNIK et al. [1970b]). Figure 8b.6 shows the Mössbauer transmission spectra of $KAu(CN)_4$ taken at a pressure of 60 kbar and after release of this pressure. The applied pressure was determined from the change of the isomer shift of metallic gold, which was also present

in the absorber (see ch. 6b for details). Both S and ΔE_Q clearly increase with pressure.

Similar high-pressure experiments have recently been performed on the aurous compounds AuCN and $KAu(CN)_2$ (PROSSER [1973], PROSSER et al. [1974]). In this work the applied pressure was determined by an improved method, utilizing the pressure dependence of the superconducting transition temperature of metallic lead.

A summary of the high-pressure results for auric and aurous compounds is presented in fig. 8b.7, where the pressure-induced changes of the electric-quadrupole splitting are plotted versus the changes of the isomer shift. In all cases the isomer shift increases with applied pressure, but striking differences are observed in the pressure-induced changes of the absolute size of ΔE_Q. For $KAuCl_4$ and $KAu(CN)_4$ the pressure-induced changes of ΔE_Q and S follow the ΔE_Q - S correlation for auric compounds. This can be seen from fig. 8b.5, where the pressure-induced changes of ΔE_Q and S in the two compounds are represented by arrows. The observed behaviour has been interpreted by BARTUNIK et al. [1970b] as resulting from an increase of the metal-ligand overlap due to the increased pressure, which leads to an increase in the atomic populations of the σ-bonding molecular orbitals on the gold ion. As discussed in the preceding section, this would result in the observed changes of ΔE_Q and S. In the case of the aurous compounds the results of the high-pressure experiments are quite different. The pressure-induced changes of ΔE_Q and S (represented by arrows in fig. 8b.4 do not follow the ΔE_Q - S correlation for aurous compounds. Therefore, with our model, the data cannot

be interpreted on the only basis of an increase of σ-bonding covalency with increasing pressure. It has been proposed by PROSSER [1973] that a predominant increase of π-bonding with pressure would explain these data qualitatively. Recent X-ray lattice constant measurements for AuCN, showing that mainly the a-axis and not the c-axis is changing with increasing pressure, have been interpreted in a similar way (PROSSER et al. [1974]).

4. Gold-Organic Compounds

During the last few years organogold[§] chemistry has received growing interest, both because of the possible technological value of some of these compounds as catalysts and because of the interesting theoretical aspects of the bonding of organic ligands to gold. The chemistry of such compounds has recently been reviewed by ARMER and SCHMIDBAUR [1970], by BÄHR and BURBA [1970], by BROWN et al. [1973], and by ROTHGERY [1974].

Mössbauer investigations of Au(I), Au(III), and mixed-valency Au(I)Au(III) complexes with olefin and acetylene ligands, and of Au(I) and Au(III) tetrazol complexes have been reported by BARTUNIK et al. [1970a] and by BARTUNIK [1974]. JARVIS et al. [1973] have published a Mössbauer study of an intermediate reaction product, viz. a methyl-gold compound containing monovalent and trivalent gold. The S and ΔE_Q values for all investigated gold-organic compounds are compiled in table 8b.3.

[§]In the present context, organogold chemistry will include all gold compounds with at least one Au-C bond, with the exception of the cyano-gold complexes.

4.1. Olefin-AuCl and Acetylene-AuCl Complexes

Complexes of the form L-AuCl, where L stands for olefin or dimethylacetylene (DMA), have been synthesized by Hüttel and his coworkers (HÜTTEL et al. [1966a; 1966b; 1972]; TAUCHNER [1974]; TAUCHNER and HÜTTEL [1974]). The results of NMR and infrared-spectroscopical work give evidence for a direct bonding of the olefin and acetylene ligands to gold.

Mössbauer experiments have been performed on compounds of this type where L is hexadecene ($C_{16}H_{32}$), octadecene ($C_{18}H_{36}$), norbornadiene (C_7H_8), cyclooctatetraene (C_8H_8), or DMA (C_4H_6). All spectra show a resolved quadrupole doublet. A typical spectrum is reproduced in fig. 8b. 8a. The isomer shifts and the quadrupole splittings in these compounds (table 8b.3) are interpreted within the framework of a concept for the bonding of olefin ligands to transition metals, which was introduced by DEWAR [1951] and CHATT and DUNCANSON [1953]. For the acetylene-metal bonding a similar model was proposed by NELSON et al. [1969]. In the Dewar-Chatt-Duncanson model, which is based on M.O. theory, σ-bonding results from an overlap of a π-orbital of the olefin with a suitable vacant hybrid orbital of the metal; similarly, π-bonds are formed by an overlap of filled hybrid orbitals of the metal with the antibonding π^*-orbitals of the olefin. In the case of Au(I), the $5d_z2$, 6s, and $6p_z$ orbitals are suitable for σ-bonding, while the $5d_{xz}$ and $6p_{x,y}$ orbitals can overlap with the antibonding π^*-2p orbitals of the olefin, which are not occupied in the free molecule. The σ-bonding leads to a ligand-to-metal charge transfer, reducing the electron density in the bonding orbitals of the

olefin ligand upon the formation of the complex. The resulting weakening of the C-C double bond has been observed through a decrease in the stretching frequency (HÜTTEL et al. [1968]). The charge transferred to the metal by σ-bonding is partly back-donated in a synergic way to the π^* orbitals of the olefin, if the energy difference between the donor orbitals of the metal and the π^* orbitals is not too large. This is thought to be the case in Au(I) complexes because of the low oxidation state of gold.

The observed isomer shift change from AuCl to olefin-AuCl is consistent with this model. A substitution of the σ-accepting and π-donating chlorine ligand by an olefin ligand with σ-donor and/or π-acceptor properties should indeed result in an increase of $\rho(0)$ (see § 3.2). NMR measurements on olefin-AuCl complexes (REINHEIMER [1967]) suggest a significant π-backbonding and a less important σ-bonding. This is consistent with the Mössbauer results and agrees with the interpretations given for other transition-metal olefin complexes (NELSON et al. [1971]).

The considerable variation in the structural dimensions of the olefin ligands in the studied compounds is not reflected in the S and ΔE_Q results. These parameters are almost solely affected by the nature of the C-C double bond, and not by other constituents of the ligand molecule, not even by those near the double bond, possibly, because these are bent away from the metal atom (NELSON et al. [1971]). There is no evidence from the Mössbauer work that in norbornadiene-AuCl both double bonds of the olefin are involved in the bonding to the metal, as has been proposed by REINHEIMER [1967] on the basis of NMR measurements. In fact, all olefin ligands in the compounds investigated seem to be monodendate.

In the case of an acetylene ligand, two π-orbitals which are perpendicular to each other and the corresponding π^*-orbitals are available for σ- and π-bonding to the metal. The $5d_z2$, 6s, and $6p_z$ orbitals of Au(I) are suitable for σ-type bonding, and the $5d_{xz,yz}$ and $6p_{x,y}$ orbitals for π-bonding. If both π-orbitals were involved in the bonding, the acetylene ligands should be better σ-donors and π-acceptors than the olefin ligands because of the lower-energy of their π-orbitals (NELSON et al. [1971]). The isomer shift of DMA-AuCl indicates, however, that the donor and acceptor properties of the acetylene ligand in this complex are similar to those of the olefin ligands. It cannot be decided from the Mössbauer results whether both π-orbitals of DMA or only one of them are used. The charge transfers in the σ and π bonds should, however, be nearly the same as in the olefin-gold bond.

4.2. Mixed-valency Complexes

Complexes of the form $(L)_nAu(I)Au(III)Cl_4$, where L stands for an olefin or acetylene ligand, and n may be 1, 2 or 3, have been synthesized by HÜTTEL et al. [1966a; 1966b; 1968; 1972]; TAUCHNER [1974]; TAUCHNER and HÜTTEL [1974]. Mössbauer experiments have been performed on $(L)_nAu_2Cl_4$ with L = norbornadiene (nor) and n = 1 to 3, with L = cyclooctatetraene (COT) and n = 1, and with L = DMA and n = 2 (BARTUNIK [1974]).

A typical spectrum is shown in fig. 8b.8b. Since the isomer shifts in the mono- and trivalent gold compounds appear to depend mainly on the immediate ligand environment of gold and only to a minor degree on atoms further remote from the gold, as e.g. cations, the interpretation of the spectra obtained for the mixed-valency compounds has

been based on a comparison with the results for Au(I) and for Au(III) compounds with olefin or acetylene and/or chlorine ligands.

The results confirmed the existence of both Au(I) and Au(III) in all the investigated complexes. The S and ΔE_Q values of $(DMA)_2Au_2Cl_4$ provided evidence for linear DMA-Au(I)-DMA bonds and for an almost unperturbed $AuCl_4^-$ unit; this interpretation received further support from chemical reaction studies (FORKL [1972]). The existence of a group $(DMA)_2Au$ would indicate a significant π-backbonding component in the gold-acetylene bond. A saturation effect in the isomer shift changes which are induced by the sequential substitution of the chlorine by acetylene ligands shows up if one compares the isomer shifts in AuCl, DMA-AuCl and $(DMA)_2Au$. Such an effect has also been noticed for other transition metal compounds with backbonding ligands (see § 3.2)

Among the mixed-valency complexes with norbornadiene ligands, $(nor)_1Au_2Cl_4$ is the only compound for which Mössbauer spectra were obtained that could be fitted unambiguously. The S values do not support a previously postulated bonding structure (REINHEIMER [1967]) characterized by nor-Au(I)-Cl and $AuCl_4^-$ units, but would rather be consistent with a bonding of the olefin ligand to the trivalent gold ion. As in square-planar olefin complexes of platinum (NELSON et al. [1971]) the C-C double bond is possibly oriented perpendicular to the plane defined by the gold and three chlorine ligands. Clearly, a determination of the crystallographic structure is desirable; it should also include a determination of the positions of the hydrogen atoms near the double bond, which might affect the gold-olefin bond (compare with § 4.3).

Studies of both the three-dimensional structure and the Mössbauer effect have been undertaken on a mixed-valency acetylene substituted methylgold compound, $(MeAuX)_2C_4F_6$, with X = tertiary phosphine (JARVIS et al. [1973]). Au(III) has been found to have a square-planar, Au(I) a linear twofold coordination. Both gold ions are cis-bound to the double bond of the C_4F_6 ligand. The isomer shifts, which were ascribed to Au(I) and Au(III), respectively, were not further discussed, however, in this paper.

4.3 Other Gold-Organic Compounds

On the basis of a gamma-resonance study of gold-chloride complexes with hexamethyldewarbenzene (HMDB) ligands, $(HMDB)HAuCl_4$ and $(HMDB)AuCl_5$, a bonding structure of the type $(HMDB)\ X^+AuCl_4^-$, where X = H, Cl has been suggested (TAUCHNER [1974]; BARTUNIK [1974]). The square-planar tetrazolato complexes Ph_4AsAuT_2 and Ph_4AsAuT_4, where T stands for (CN_4R), with $R = C_6H_{11}$, were synthesized by BECK and FEHLHAMMER [1967]. A structure determination of the very similar compound $Ph_4AsAu(CN_4R')$, with $R' = i\text{-}C_3H_7$, proved that the tetrazole ligand directs its CN group towards the gold; the Au-C bond-length turned out to be essentially the same as in the cyanide complex $H_5O_2Au(CN)_4$ (FEHLHAMMER and DAHL [1972]). One might therefore expect that the electron donor and acceptor properties of the tetrazole ligand are comparable to those of the cyanide ligand. For both oxidation states (+1 and +3) of gold, the isomer shifts in the tetrazolato complexes, however differ greatly from those measured for the cyanide complexes and fall in fact into the range of those for the halides (BARTUNIK et al. [1970a]). Taking the S values alone, one would have

to assume that the tetrazole ligand has σ-acceptor and/or π-donor properties. The fact that no quadrupole splitting was observed in both tetrazolato-gold complexes (which does not fit into the ΔE_Q-S correlation) indicates that the bonding between the gold and the CN group of the ligand may be influenced by atoms (especially hydrogen atoms), which are close to the metal.

Table 8b.1. Compilation of isomer shifts, S, and electric-quadrupole splittings, ΔE_Q, for inorganic gold compounds; S is taken relative to a platinum metal source. The numbers in parentheses represent the statistical uncertainties in units of the last digit. In order to refer these isomer shifts to metallic gold, + 1.25(2)mm/s have to be added to the tabulated values of S.

compound	S (mm/s)	ΔE_Q (mm/s)	Ref.
	monovalent compounds		
AuCl	-1.39 (3)	4.56 (9)	a,b,(c,d)
AuBr	-1.47 (1)	4.23 (4)	b,(d)
AuI	-1.26 (6)	3.94 (8)	a,b,(c,d)
AuCN	2.30 (4)	7.95 (10)	a,f,h,(b,c)
$KAu(CN)_2$	3.13 (5)	10.20 (10)	a,f,h,(b)
$Ph_4AsAu(N_3)_2$	1.43 (5)	6.84 (10)	a
Ph_3PAuMe	4.93 (4)	10.35 (6)	c
Ph_3PAuCN	3.9 (2)	10.5 (2)	c
$Ph_3PAuOCOMe$	3.3 (2)	7.6 (2)	c
Ph_3PAuN_3	3.3 (2)	8.4 (2)	c
$C_6F_5Ph_2PAuCl$	2.93 (3)	7.87 (4)	c
Ph_3PAuCl	2.96 (7)	7.47 (13)	c
Ph_3PAuBr	2.76 (6)	7.40 (10)	c
$Ph_3PAsAuCl$	1.92 (3)	7.00 (7)	c
C_5H_5NAuCl	1.7 (1)	6.4 (2)	c
Me_2SAuCl	1.26 (2)	6.42 (3)	c
Ph_3PAuF	1.24 (6)	8.3 (1)	c

Table 1 (continued)

trivalent compounds

AuF_3	-1.06 (2)	2.72 (2)	b,g,(e)
$KAuF_4$	-0.04 (2)	0.00 (5)	c, (e)
$CsAuF_4$	0.09 (2)	0.75 (4)	a
$RbAuF_4$	0.05 (2)	0.17 (35)	a
BrF_2AuF_4	-0.69 (2)	1.82 (2)	b
$KAuI_4$	0.43 (5)	1.28 (10)	a,(c)
$AuBr_3$	0.48 (7)*	0.0 (1)*	a
	0.79 (7)*	1.27 (2)*	b
	0.18 (10)*	1.8 (2)*	c
$KAuBr_4$	0.64 (4)	1.13 (5)	a,b,(c,d)
$Ph_4AsAuBr_4$	0.85 (11)	1.5 (2)	c
$AuCl_3$	0.57 (9)	0.75 (8)	b,(c,d)
$HAuCl_4 \cdot 4H_2O$	0.66 (4)	0.94 (8)	a,(c)
$NaAuCl_4 \cdot 2H_2O$	0.81 (5)	1.21 (10)	a,(c)
$KAuCl_4$	0.81 (3)	1.11 (6)	a,(b-e)
NH_4AuCl_4	0.87 (3)	1.18 (6)	a,(c)
$(C_4H_9)_4NAuCl_4$	1.02 (6)	1.31 (14)	a
$Ph_4AsAuCl_4$	1.09 (4)	1.88 (7)	c
$CsAuCl_4$	-0.4 (5)	0.0 (1)	e
$C_{12}H_{10}N_2AuCl_3$	1.32 (3)	1.94 (6)	a
Ph_3PAuCl_3	2.06 (4)	3.25 (8)	c
$C_5H_5NAuCl_3$	1.45 (5)	0.0 (1)	c
Me_2SAuCl_3	1.26 (5)	2.20 (8)	c
$p\text{-}MeC_6H_4NCAuCl_3$	0.75 (5)	2.00 (9)	c

Table 1 (continued)

$KAu(SCN)_4$	1.63 (7)	2.04 (14)	a
$Ph_4AsAu(N_3)_4$	1.66 (5)	2.89 (10)	a
$Au_2O_3 \cdot 2H_2O$	1.31 (8)*	1.69 (16)*	a
	0.63 (8)*	2.3 (2)*	c
	0.94 (1)*	1.68 (4)*	b
Li_3AuO_3	1.95 (4)	2.27 (8)	a
Na_3AuO_3	2.45 (4)	3.02 (8)	a
AuO(OH)	1.38 (3)	1.71 (6)	a
$Na_3Au(S_2O_3)_2$	0.72 (29)	7.08 (4)	b
$KAu(CN)_2Cl_2$	2.56 (2)	5.26 (2)	b
$KAu(CN)_2Br_2$	2.68 (4)	5.40 (8)	a,b
$KAu(CN)_2I_2$	2.78 (6)	5.87 (3)	b
$KAu(CN)_4$	4.03 (6)	6.86 (12)	a
$(C_2H_5)_4NAuS_4C_4(CN)_4$	3.26 (7)	1.97 (6)	b
	pentavalent compounds		
$CsAuF_6$	2.39 (2)	0.00 (5)	g
$Xe_2F_{11}AuF_6$	2.28 (1)	0.00 (5)	g
XeF_5AuF_6	2.31 (2)	0.00 (5)	g

References:

a) BARTUNIK et al. [1970a]
b) FALTENS and SHIRLEY [1970]
c) CHARLTON and NICHOLS [1970]
d) SHIRLEY et al. [1964a]
e) ROBERTS et al. [1962]
f) POTZEL and PERLOW [1972]
g) KAINDL et al. [1973]
h) PFEIFFER et al. [1973]

*The discrepancy between various authors may be due to the chemical instability of the compound.

Table 8b.2. Atomic electric-field gradients q_{zz} of various p and d orbitals

orbital	q_{zz}
p_z	$-4/5 \langle r^{-3} \rangle_p$
p_x	$+2/5 \langle r^{-3} \rangle_p$
p_y	$+2/5 \langle r^{-3} \rangle_p$
d_{z^2}	$-4/7 \langle r^{-3} \rangle_d$
d_{xz}	$-2/7 \langle r^{-3} \rangle_d$
d_{yz}	$-2/7 \langle r^{-3} \rangle_d$
$d_{x^2-y^2}$	$+4/7 \langle r^{-3} \rangle_d$
d_{xy}	$+4/7 \langle r^{-3} \rangle_d$

Table 8b.3. Summary of results for isomer shift, S, and electric-quadrupole splitting, ΔE_Q, for monovalent, trivalent, and mixed-valency gold-organic compounds. The isomer shifts are given with respect to a Pt metal source. In order to refer them to metallic gold one has to add 1.25(2) mm/s to the listed values of S.

compound	S (mm/s)	ΔE_Q (mm/s)	Ref.
monovalent compounds			
$C_{10}H_{12}AuCl$	0.83 (2)	6.04 (4)	a
$C_{16}H_{32}AuCl$	1.03 (3)	6.29 (6)	a
$C_{18}H_{36}AuCl$	0.91 (3)	6.41 (6)	a
C_4H_6AuCl	0.79 (2)	6.38 (4)	b
C_7H_8AuCl	0.96 (2)	6.02 (4)	b
C_8H_8AuCl	0.52 (3)	5.96 (5)	b
Ph_4AsAuT_2	-1.06 (3)	0.0 (1)	a
trivalent compounds			
$[C_{12}H_{19}]AuCl_4$	0.98 (4)	1.40 (7)	b
$[C_{12}H_{18}Cl]AuCl_4$	1.15 (2)	1.61 (4)	b
$C_{12}H_{22}AuCl$	3.71 (3)	3.53 (5)	b
Ph_4AsAuT_4	0.19 (2)	0.0 (1)	a

mixed-valency compounds	Au(I)	Au(III)	Au(I)	Au(III)	
$C_7H_8Au_2Cl_4$	-0.42 (4)	2.06 (4)	4.00 (8)	3.52 (7)	b
$(C_4H_6)_2Au_2Cl_4$	1.46 (3)	0.97 (2)	6.74 (6)	1.37 (4)	b
$C_8H_8Au_2Cl_4$	-0.72 (3)	0.67 (2)	5.20 (6)	0.90 (4)	b

References:
a) BARTUNIK et al. [1970a]
b) BARTUNIK [1974]

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Figure Captions:

Fig. 8b.1. Decay scheme of ^{197}Pt after LEDERER et al. [1967].

Fig. 8b.2. Isomer shifts of Au(I), Au(III), and Au(V) compounds with respect to Au(Pt).

Fig. 8b.3. Isomer shifts for monovalent, trivalent, and pentavalent gold complexes with "innocent" ligands. The shifts are given with respect to Au(Pt).

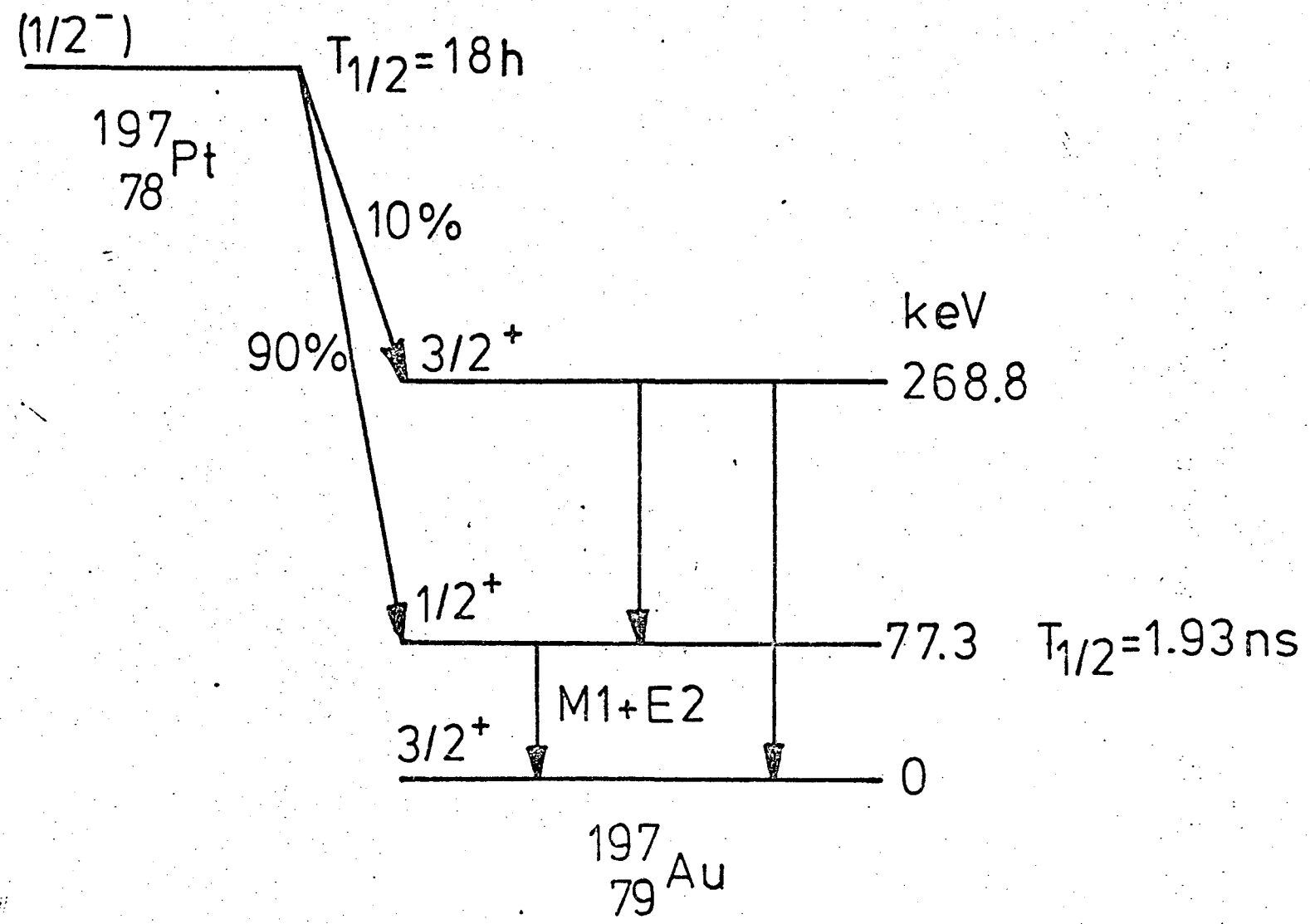
Fig. 8b.4. Relation between ΔE_Q and S for aurous compounds. The arrows represent pressure-induced changes of ΔE_Q and S (see § 3.4).

Fig. 8b.5. Relation between ΔE_Q and S for auric compounds. The arrows represent pressure-induced changes of ΔE_Q and S (see § 3.4).

Fig. 8b.6. Mössbauer absorption spectra of $KAu(CN)_4$ taken at a pressure of about 60 kbar and upon release of pressure. The position of the resonance in Au metal, measured simultaneously, yielded the value of the applied pressure.

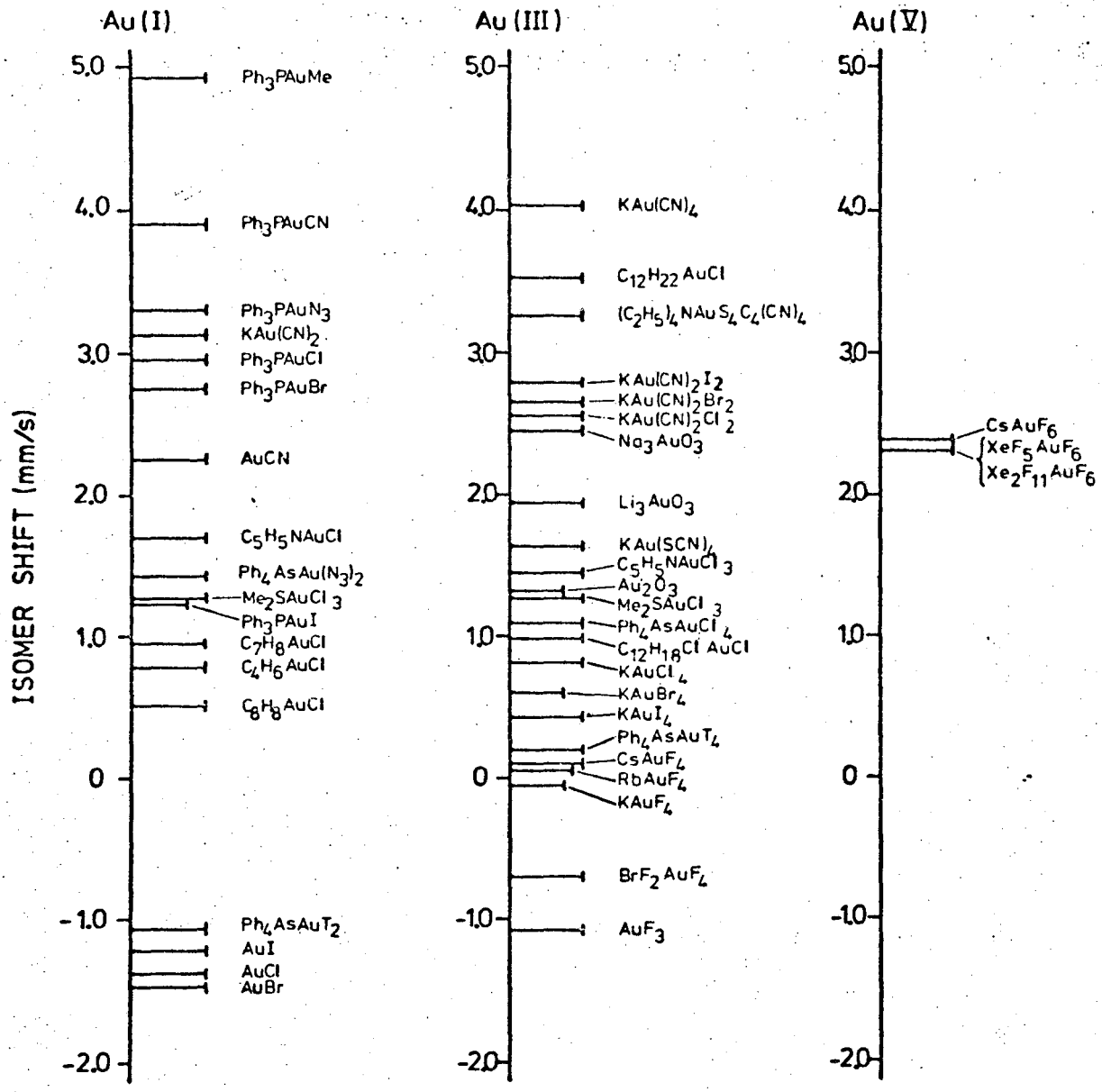
Fig. 8b.7. Change in isomer shift and electric-quadrupole splitting for aurous and auric compounds as a function of applied pressure (P). The number on each data point represents the applied pressure in units of kbar.

Fig. 8b.8. Mössbauer absorption spectra for (DMA) . AuCl (a) and $(DMA)_2Au_2Cl_4$(b).



XBL 749-1678

Fig. 8b.1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Au (III)
Au (V)
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3.0
2.0
1.0
0
-1.0
-2.0
Ph3PAuMe
Ph3PAuCN
Ph3PAuN3
KAu(CN)2
Ph3PAuCl
Ph3PAuBr
AuCN
C5H5NAuCl
Ph4AsAu(N3)2
Me2SAuCl3
Ph3PAuI
C7H8AuCl
C4H6AuCl
C8H8AuCl
Ph4AsAuT2
AuI
AuCl
AuBr
KAu(CN)4
C12H22AuCl
(C2H5)4NAuS4C4(CN)4
KAu(CN)2I2
KAu(CN)2Br2
KAu(CN)2Cl2
Na3AuO3
Li3AuO3
KAu(SCN)4
C5H5NAuCl3
Au2O3
Me2SAuCl3
Ph4AsAuCl4
C12H18ClAuCl
KAuCl4
KAuBr4
KAuI4
Ph4AsAuT4
CsAuF4
RbAuF4
KAuF4
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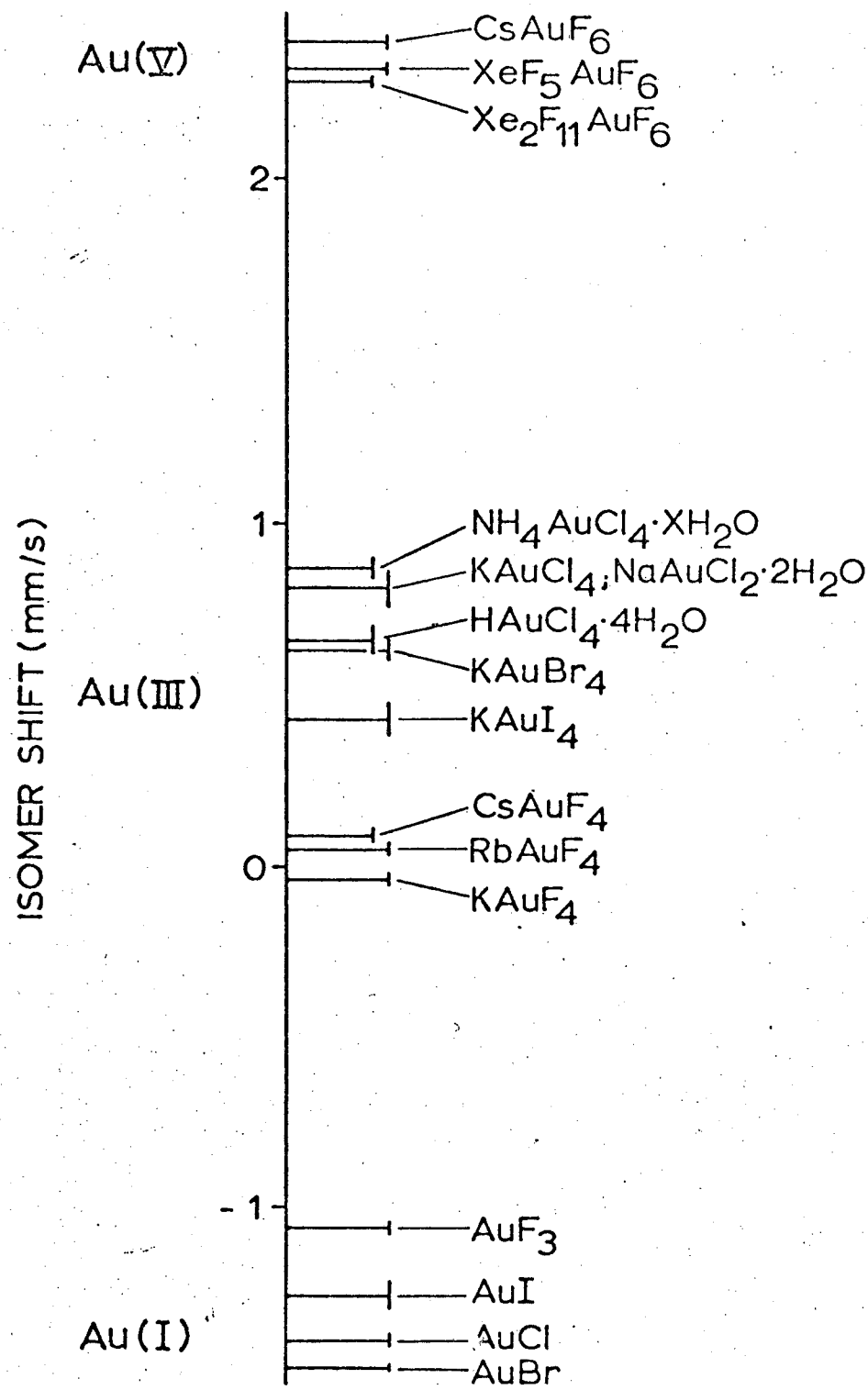
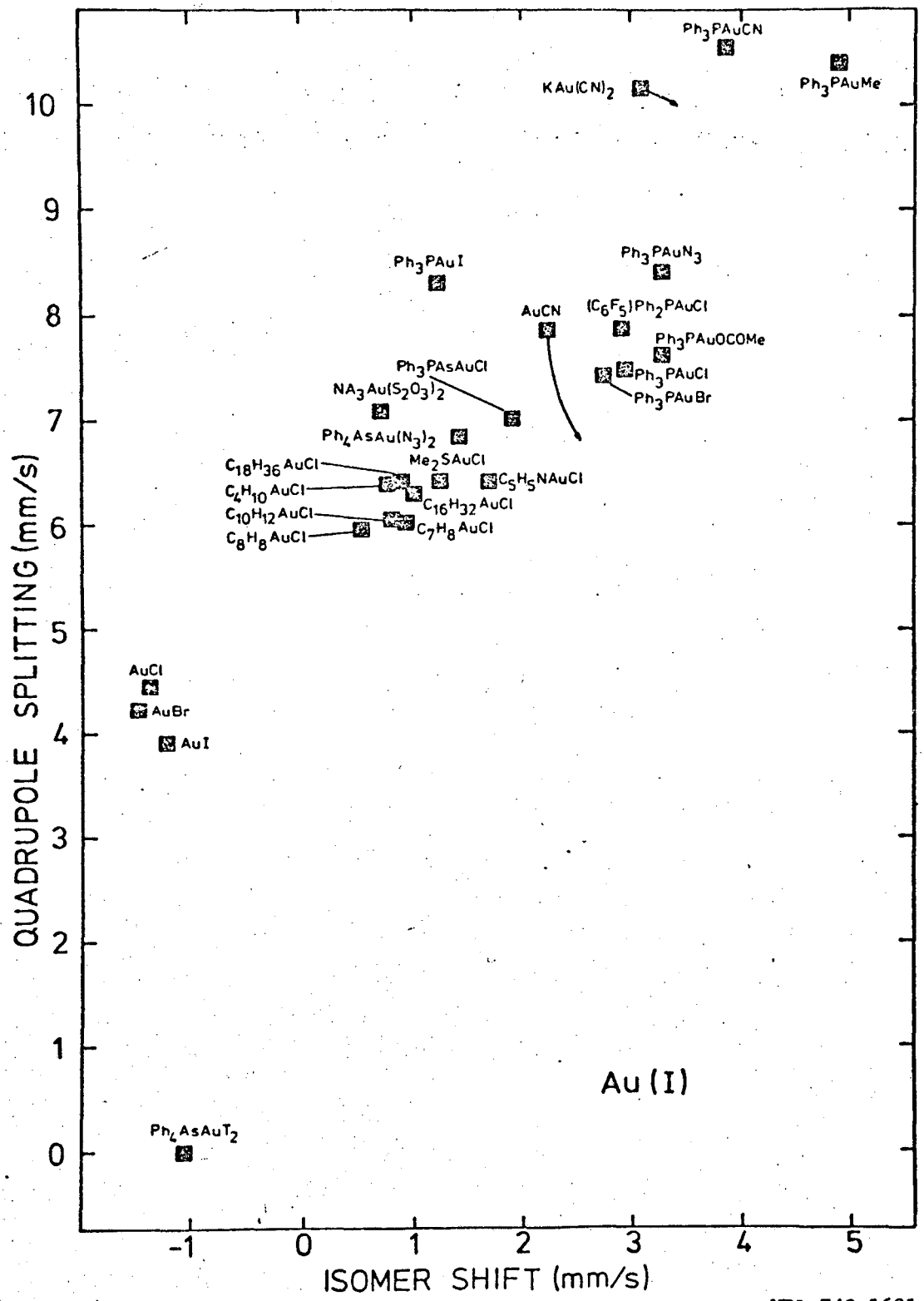
AuF3
CsAuF6
XeF5AuF6
Xe2F11AuF6
XBL 749-1679

Fig. 8b. 2



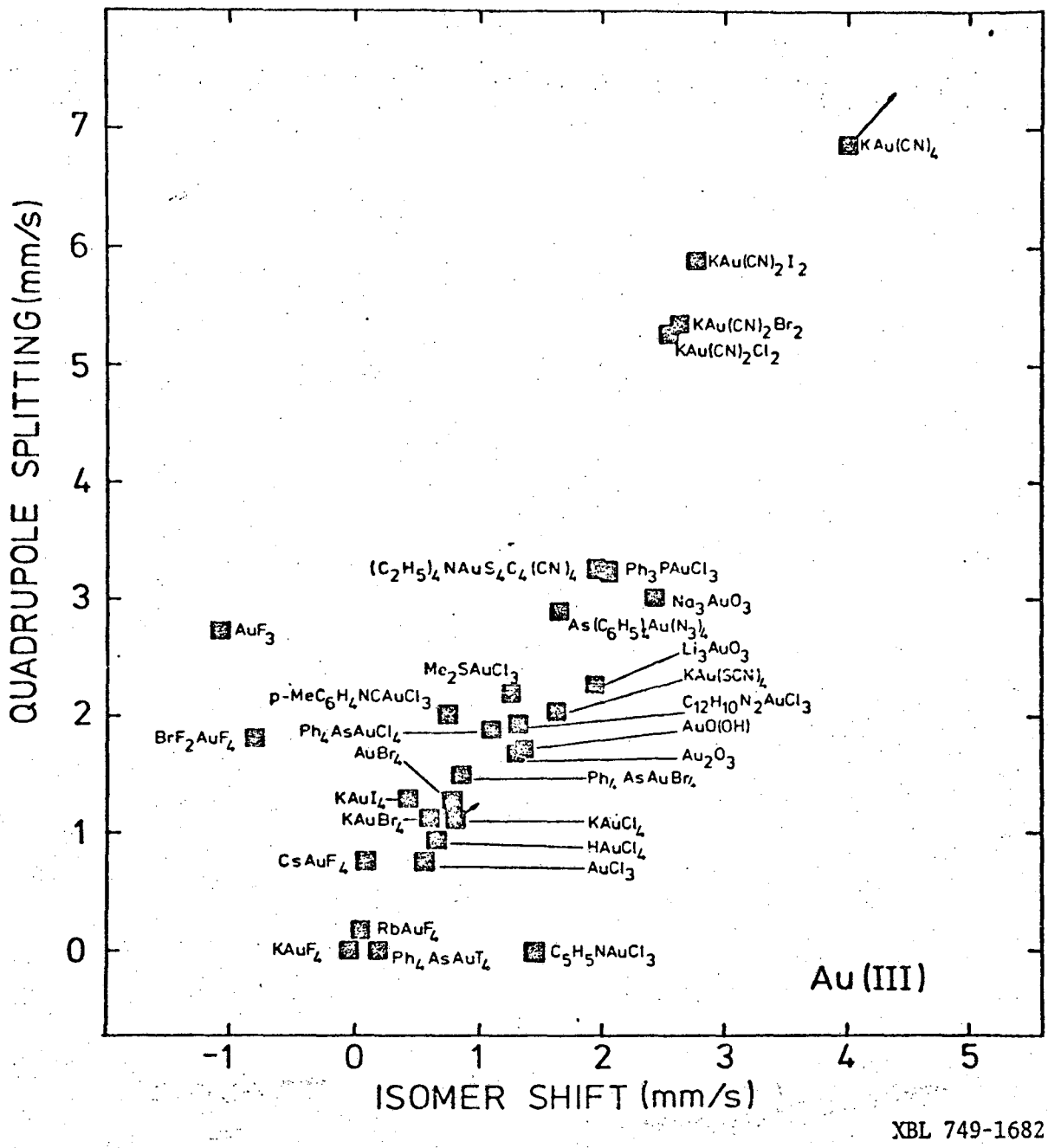
XBL 749-1680

Fig. 8b.3



XBL 749-1681

Fig. 8b.4


QUADRUPOLE SPLITTING (mm/s)
ISOMER SHIFT (mm/s)
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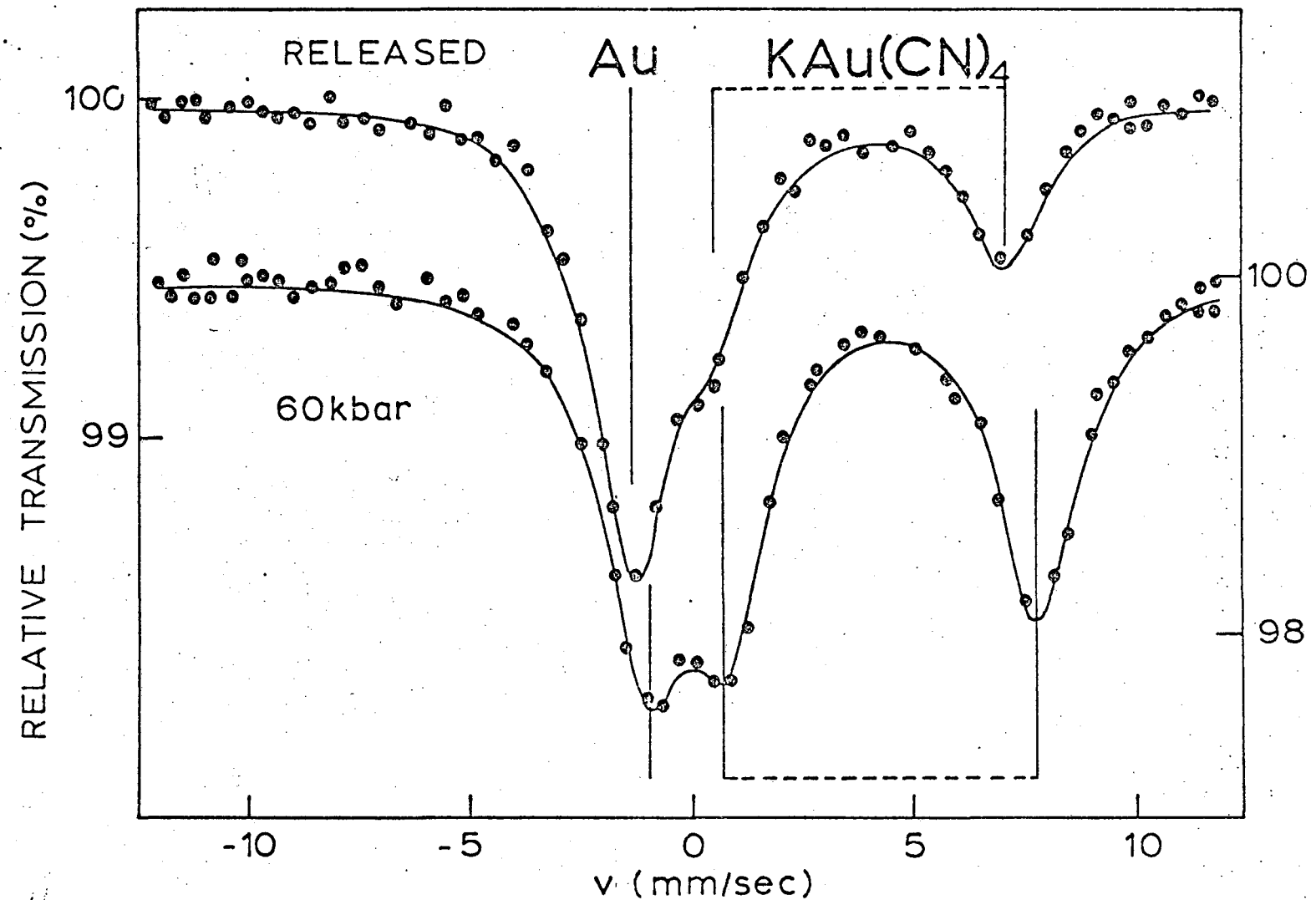
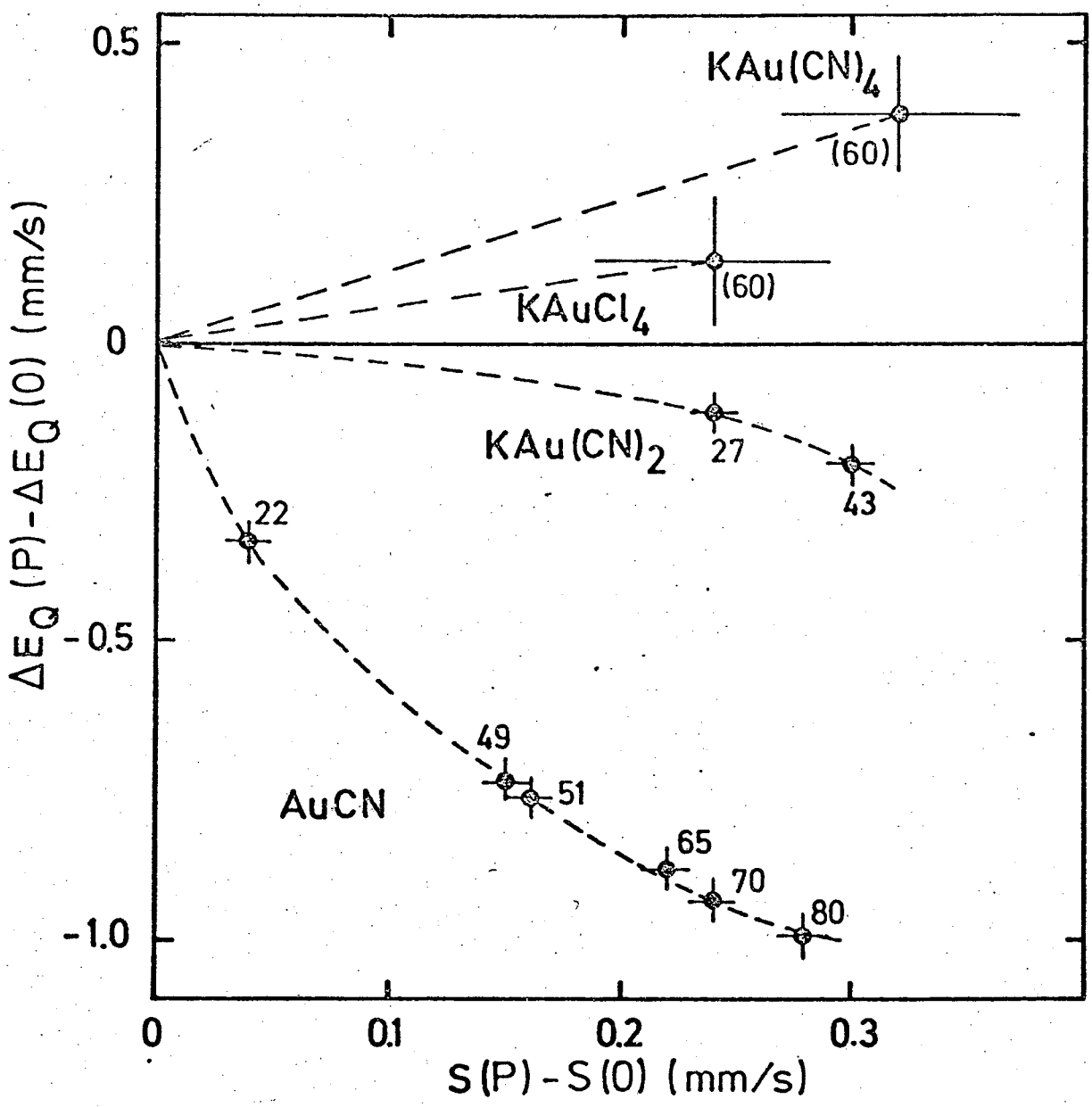
KAu(CN)2Br2
KAu(CN)2Cl2
(C2H5)4NAuS4C4(CN)4
Ph3PAuCl3
Na3AuO3
As(C6H5)4Au(N3)4
Li3AuO3
KAu(SCN)4
C12H10N2AuCl3
AuO(OH)
Au2O3
Ph4AsAuBr4
AuF3
Me2SAuCl3
p-MeC6H4NCAuCl3
Ph4AsAuCl4
BrF2AuF4
AuBr4
KAuI4
KAuBr4
KAuCl4
HAuCl4
AuCl3
CsAuF4
RbAuF4
KAuF4
Ph4AsAuT4
C5H5NAuCl3
XBL 749-1682

Fig. 8b.5



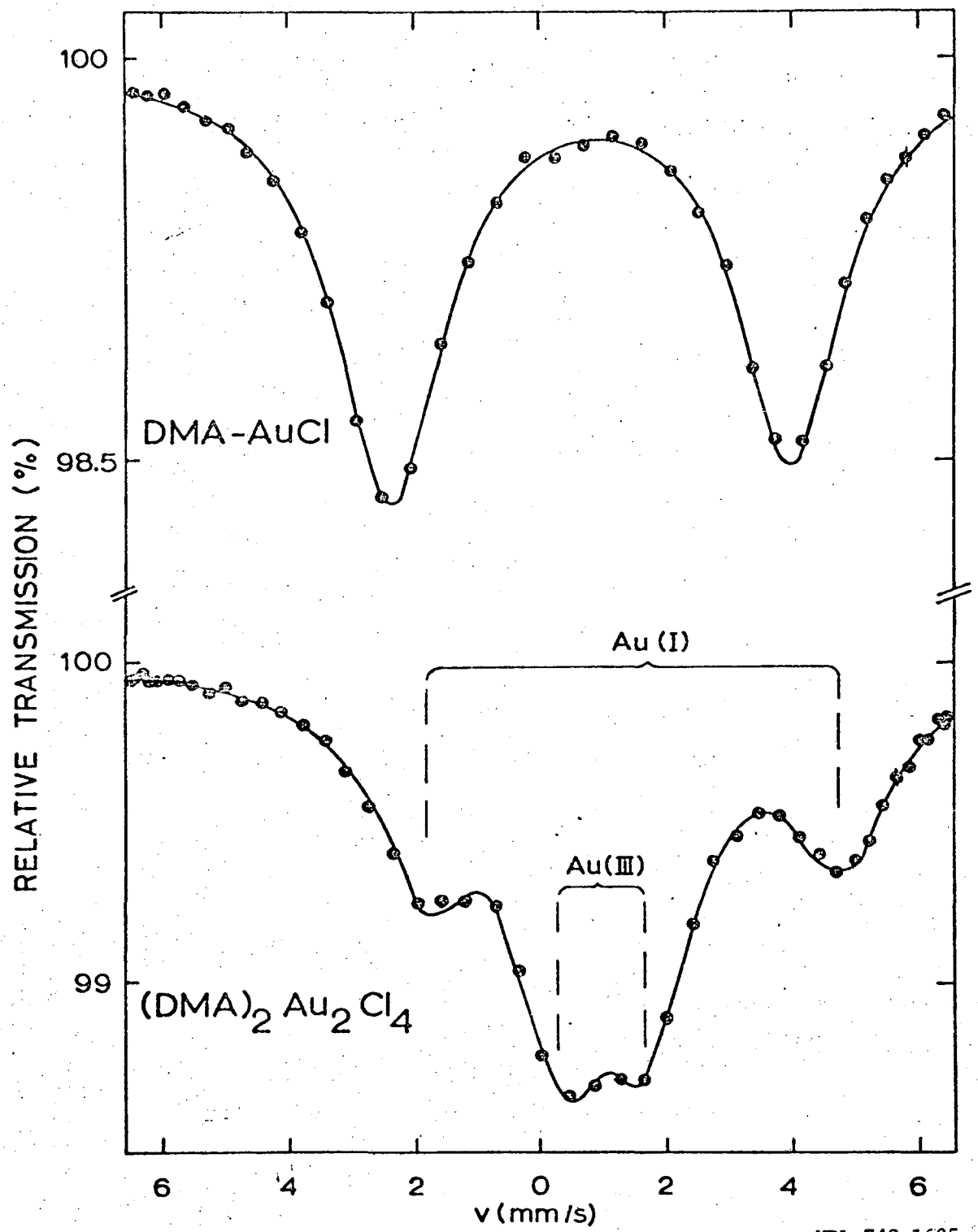
XBL 749-1683

Fig. 8b.6



XBL 749-1684

Fig. 8b. 7



XBL 749-1685

Fig. 8b.8

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