

## Structure and Bonding of Gold(I) and Gold(III) Nucleosides Studied by $^{197}\text{Au}$ Mössbauer Spectroscopy

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$^{197}\text{Au}$  Mössbauer spectra of the series of complexes of gold(I),  $\text{Au}(\text{nucl})_2\text{Cl}$  and gold(III),  $\text{Au}(\text{nucl})\text{Cl}_3$ ,  $\text{Au}(\text{nucl} - \text{H}^+)\text{Cl}_2$  and  $\text{Au}(\text{nucl})_2\text{Cl}_3$  were measured at 4.2 K, (nucl = nucleoside, e.g. guanosine(guo), inosine(ino), triacetylguanosine(trguo) and triacetylinosine(trino)). It is concluded from the spectra that the gold(I) nucleosides have linear  $\text{ClAuN}$  coordination, with one coordinated nucleoside molecule per gold(I) ion, bound via the N(7) atom. The  $\sigma$ -donor strength of the guo ligand is somewhat higher than that of the ino ligand. The complexes  $\text{Au}(\text{ino})\text{Cl}_3$  and  $\text{Au}(\text{guo})\text{Cl}_3$ , in the series  $\text{Au}(\text{nucl})\text{Cl}_3$ , have significantly higher IS and QS values than the corresponding complexes with the triacetylnucleosides,  $\text{Au}(\text{trino})\text{Cl}_3$  and  $\text{Au}(\text{trguo})\text{Cl}_3$ . This may be explained by a weak O(6)-interaction with gold(III), in a nearly trigonal bipyramidal configuration in the former case and by the presence of the strongly electron withdrawing acetyl groups in the latter, which reduces the donor strength of their N(7) atoms. The complexes of the  $\text{Au}(\text{nucl} - \text{H}^+)\text{Cl}_2$  series all appear to have a polymeric structure. The gold(III) ion is bound to the N(7) atom and the O(6) or the N(1) atom of the nucleosides. Finally, the Mössbauer spectra of the series  $\text{Au}(\text{nucl})_2\text{Cl}_3$  can only be explained by assuming approximately octahedral  $\text{AuN}_2\text{Cl}_4$  structures, with bridging chlorine atoms.

### Introduction

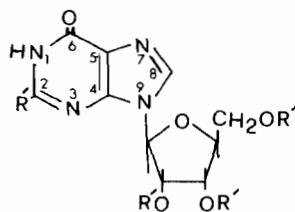
Many investigations have been carried out on the synthesis and characterization of organo-gold compounds [1]. In these compounds the possible formal

valence states of gold are the I and the III states. Usually gold(I) is coordinated linearly to two neighbor atoms, although three and four coordinated complexes have also been found [1–3]. Gold(III) complexes usually have a four coordinated square planar configuration [1], although examples of higher coordination numbers have been reported [4].

The coordination compounds of gold are also important and interesting for their biological and medicinal applications. For example, gold(III) complexes have been reported to possess antitumor activity [5], while the antiarthritic activity of gold(I) sulfur complexes [6] is well known. There are many other biological applications of gold compounds [6] and interesting recent developments [7–10]. In an earlier paper, the synthesis of various gold(I) and gold(III) nucleoside complexes was described [11]. Based on elemental analysis, conductivity measurements, i.e.,  $^1\text{H}$  nmr and esr measurements, possible structures for the isolated complexes were suggested and the binding sites of nucleosides with gold were determined [11]. The N(7) site of the nucleosides (Fig. 1) is the main preferred binding site in all cases, with both gold(I) and gold(III), as the  $^1\text{H}$  nmr spectra of the complexes in  $\text{DMSO-d}_6$  show. In a few cases the O(6) and/or N(1) atoms may serve as a second binding site of the nucleosides to gold, besides N(7), as followed from i.r. measurements, performed on the solid compounds [11].

In this paper we present  $^{197}\text{Au}$  Mössbauer measurements on the series of gold–nucleoside complexes with the nucleosides inosine, guanosine, triacetylinosine and triacetylguanosine (Fig. 1). These measurements provide structural and bonding information on the local environment of the gold atoms in the solid state. The Mössbauer hyperfine parameters are rather sensitive to changes in gold

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$R=H$ , $R'=H$	inosine (ino)
$R=NH_2$ , $R'=H$	guanosine (guo)
$R=H$ , $R'=OCOCH_3$	triacetylinosine (trino)
$R=NH_2$ , $R'=OCOCH_3$	triacetylguanosine (trguo)

Fig. 1. The structures of the nucleoside ligands used in the synthesis of gold(I) and gold(III) nucleosides. In the deprotonated nucleosides one  $H^+$  ion has been removed from the N(1) atom.

coordination. Although there is a lack of adequate calculations for complexes with heavy elements like gold and the observed hyperfine interactions cannot be explained quantitatively, trends in electro-negativity or covalency can be observed quite easily in homologous series of complexes. Moreover, in many cases, information can be obtained from measured Mössbauer parameters, by comparing them with the parameters of similar compounds of known structure [12]. Only a few Mössbauer experiments have been reported thus far on complexes with gold–nitrogen bonds and the results of these studies are included in the interpretation of our results.

### Experimental

The synthesis of the complexes  $Au(\text{nucl})_2Cl$ ,  $Au(\text{nucl})_2Cl_3$ ,  $Au(\text{nucl})Cl_3$  and  $Au(\text{nucl} - H^+)Cl_2$  has been described previously [11]. Samples of 50 to 150 mg of these complexes were pressed in lucite boxes; the effective thickness,  $t_a$ , of the samples ranged between 1 and 2. The  $^{197}\text{Mössbauer}$  measurements were carried out in a liquid helium bath cryostat at 4.2 K, with a spectrometer arrangement described elsewhere [12]. The integrating counting technique, detecting the total spectrum of transmitted gamma-rays, was used [13]. The samples with the highest effective thicknesses could be measured in about twenty minutes, in this way. The source used was a 70 mg disk of platinum, enriched to 97%  $^{196}\text{Pt}$ , by placing it in a high neutron flux for 24 hours, yielding a source of about 200 mCi initially.

The resulting Mössbauer spectra were fitted after folding of the two spectrum halves, with sets of Lorentzian lines. Most spectra were simulated with a set of two independent lines.

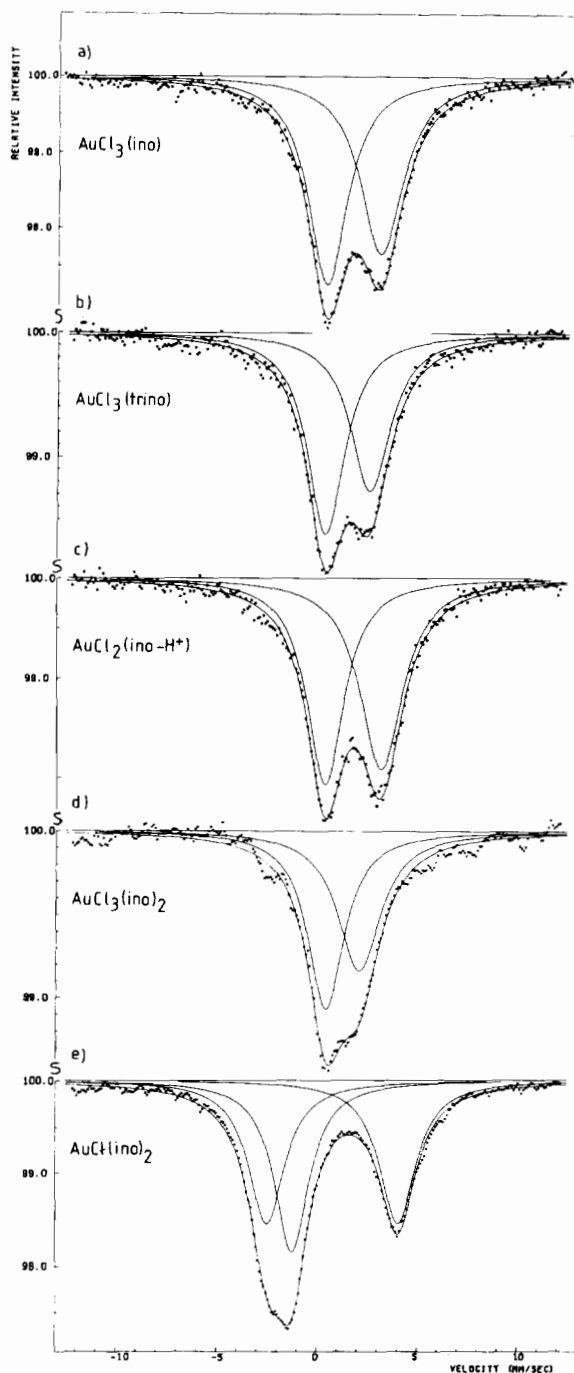


Fig. 2. Mössbauer spectra of gold (tr)inosine compounds. The solid lines represent least squares fits to the individual lines and the total spectrum. a)  $AuCl_3(\text{ino})$ ; b)  $AuCl_3(\text{trino})$ ; c)  $AuCl_2(\text{ino} - H^+)$ ; d)  $AuCl_3(\text{ino})_2$ ; e)  $AuCl(\text{ino})_2$ .

### Results

In Fig. 2 the measured Mössbauer spectra of all synthesized gold inosine complexes and  $Au(\text{trino})Cl_2$  are given. The spectra in Fig. 2a,b,c,d have

TABLE I.  $^{197}\text{Au}$  Mössbauer Hyperfine Parameters of Various Gold–Nucleoside Complexes.

Compound	IS (mm/s) <sup>a</sup>	QS (mm/s)	$\Gamma_1$ (mm/s)	$\Gamma_2$ (mm/s)
1. AuCl(ino) <sub>2</sub> <sup>b</sup>	0.80(2)	6.54(2)	2.19(2)	2.19(2)
2. AuCl(guo) <sub>2</sub>	1.14(10)	6.44(10)	4.60(10)	4.60(10)
3. AuCl <sub>3</sub> (guo)	1.88(1)	2.89(2)	2.40(10)	2.70(10)
4. AuCl <sub>3</sub> (ino)	1.71(1)	2.55(1)	2.00(10)	2.50(10)
	1.72(2)	2.68(2)	2.40(10)	2.60(10)
5. AuCl <sub>3</sub> (trguo)	1.54(2)	2.35(2)	2.30(10)	2.40(10)
6. AuCl <sub>3</sub> (trino)	1.46(2)	2.21(2)	2.30(10)	2.50(10)
7. AuCl <sub>2</sub> (guo – H <sup>+</sup> )	1.85(2)	2.94(2)	2.50(10)	2.70(10)
8. AuCl <sub>2</sub> (ino – H <sup>+</sup> )	1.79(2)	2.79(2)	2.20(10)	2.60(10)
9. AuCl <sub>2</sub> (trguo – H <sup>+</sup> )	1.77(2)	2.76(2)	2.50(10)	2.80(10)
10. AuCl <sub>3</sub> (guo) <sub>2</sub> <sup>c</sup>	1.10(10)	1.50(10)	2.00(10)	2.00(10)
11. AuCl <sub>3</sub> (ino) <sub>2</sub>	1.22(2)	1.60(2)	2.30(10)	2.30(10)
	1.29(3)	1.66(3)	2.20(10)	2.60(10)
12. AuCl <sub>3</sub> (trguo) <sub>2</sub>	0.99(2)	1.51(2)	2.30(10)	3.10(10)
13. AuCl <sub>3</sub> (trino) <sub>2</sub>	1.03(2)	1.44(2)	2.20(10)	2.50(10)

<sup>a</sup>Relative to  $^{197}\text{Pt}/^{196}\text{Pt}$ . <sup>b</sup>The spectrum has an additional single line component due to metallic gold with IS =  $-1.21$  mm/s,  $\Gamma = 2.09$  mm/s. <sup>c</sup>The spectrum has an additional component, a gold(III) quadrupole pair with IS =  $1.8(1)$  mm/s, QS =  $3.4(4)$  mm/s,  $\Gamma_1 = 3.6(3)$  mm/s,  $\Gamma_2 = 3.6(3)$  mm/s.

small quadrupole splittings, characteristic of gold(III). The spectrum in Fig. 2e has a quadrupole splitting characteristic of gold(I).

The gold(III) spectra are quite asymmetric quadrupole doublets. However, in almost all cases the areas of the two lines are equal within the error ranges. This phenomenon is indicative of small variations in the local environment of the gold(III) atoms [3]. This results in the observed asymmetry effect, because of the linear relationship of the isomer shift (IS) and the quadrupole splitting (QS).

The spectrum of Au(ino)<sub>2</sub>Cl has an additional component originating from metallic gold. The compound is very light sensitive and apparently partly decomposes during sample preparation. The hyperfine parameters of all measured samples have been collected in Table I.

For some less stable complexes, the measurements were repeated using a second sample to avoid erroneous conclusions. For example, the spectrum of [Au(guo)<sub>2</sub>Cl<sub>2</sub>]Cl is a superposition of two spectral components. The parameters of the second component resemble those of Au(nucl – H<sup>+</sup>)Cl<sub>2</sub>, which is a possible decomposition product in the presence of small amounts of water [11].

## Discussion

### Gold(I) Complexes

The Mössbauer parameters of both gold(I) complexes Au(ino)<sub>2</sub>Cl and Au(guo)<sub>2</sub>Cl suggest that gold-

(I) has linear coordination via two  $sp_z$  hybrid orbitals [14, 15], because they are in the range of values found for linear gold(I) compounds, coordinated to N and/or Cl ligands (See Table I, Fig. 3 and the references in the accompanying Table).

It is known that both IS and QS increase with increasing  $\sigma$ -donor strength of the ligands or decrease with their increasing electronegativity [14–16]. Thus the Cl–Au–Cl type complexes are found at low IS and QS values (IS < 0.7 mm/s), whereas the N–Au–N type complexes are found at higher values (IS > 1.4 mm/s). Because of the average environment rule, the Cl–Au–N type complexes are expected to fall in the intermediate region [14, 16]. Figure 3 includes all the types of gold complexes mentioned above and it is evident that the complexes under study have IS and QS values comparable to those of Au(C<sub>5</sub>H<sub>5</sub>N)Cl and Au[NH(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]Cl [14]. Therefore the Au(nucl)<sub>2</sub>Cl complexes are expected to be linear like the former two, with the gold(I) ion coordinated to chlorine and one of the nucleosides, through N(7) [11]. From Fig. 3 it is also evident that the  $\sigma$ -donor strength to the  $6s6p_z$  of gold(I) is stronger in guanosine than in inosine. The QS of the guanosine complex is slightly less, but the error range is rather large. The stronger  $\sigma$ -donor capacity is most probably due to the NH<sub>2</sub> group attached to C(2) in guanosine. This is also in agreement with the greater tendency of this base to coordinate to the isoelectronic Pt(II), as compared to other purine and pyrimidine bases [17].

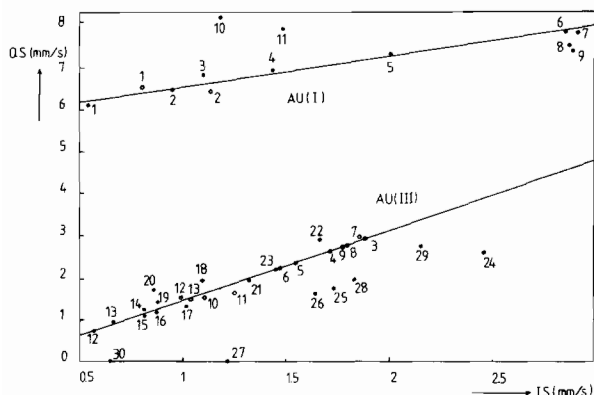


Fig. 3. Plot of QS values versus IS values of compounds measured by various authors (●), also represented in the accompanying table. The data published in this paper (Table I) are indicated with open circles (○). The numbers correspond with the numbers of the compounds in the tables. The solid lines are least squares fittings of data points for linear gold(I) complexes and square planar gold(III) complexes, with the assumptions explained in the text.

Compound	IS (mm/s)	QS (mm/s)	Reference
1. [AuCl <sub>2</sub> ][AsPh <sub>4</sub> ]	0.54	6.13	14
2. AuClNH(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	0.95	6.48	14
3. AuClC <sub>5</sub> H <sub>5</sub> N	1.10	6.75	14
4. [Au(N <sub>3</sub> ) <sub>2</sub> ][AsPh <sub>4</sub> ]	1.43	6.84	19
5. [Au(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ][PF <sub>6</sub> ]	2.01	7.32	19
6. [Au(pip) <sub>2</sub> ][PF <sub>6</sub> ]	2.86	7.88	19
7. [Au(pip) <sub>2</sub> ][Cl]	2.92	7.87	15
8. AuClPPh <sub>3</sub>	2.87	7.53	19
9. AuIPPh <sub>3</sub>	2.89	7.36	16
10. AuIPPh <sub>3</sub>	1.18	8.19	15
11. AuI(PPh <sub>3</sub> ) <sub>2</sub>	1.48	7.87	15
12. AuCl <sub>3</sub>	0.57	0.75	20
13. HAuCl <sub>4</sub> ·4H <sub>2</sub> O	0.66	0.94	19
14. NaAuCl <sub>4</sub> ·2H <sub>2</sub> O	0.81	1.21	19
15. KAUCl <sub>4</sub>	0.81	1.11	19
16. NH <sub>4</sub> AuCl <sub>4</sub>	0.87	1.18	19
17. (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NAuCl <sub>4</sub>	1.02	1.31	19
18. [AsPh <sub>4</sub> ][AuCl <sub>4</sub> ]	1.09	1.88	22
19. KAUCl <sub>4</sub> ·2H <sub>2</sub> O	0.87	1.40	23
20. NH <sub>4</sub> AuCl <sub>4</sub> ·xH <sub>2</sub> O	0.86	1.70	24
21. C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> AuCl <sub>3</sub>	1.32	1.94	19
22. [AsPh <sub>4</sub> ][Au(N <sub>3</sub> ) <sub>4</sub> ]	1.66	2.89	19
23. C <sub>5</sub> H <sub>5</sub> NAuCl <sub>3</sub>	1.45	—	21
24. [Au(oxine) <sub>2</sub> ] <sup>+</sup>	2.42	2.64	4
25. Au(oxine)Cl <sub>2</sub>	1.69	1.72	4
26. Au(5-Cl-oxine)Cl <sub>2</sub>	1.60	1.62	4
27. [Au(phen)Cl <sub>2</sub> ][Cl]	1.17	—	4
28. [Au(phen)Cl <sub>2</sub> ][ClO <sub>4</sub> ]	1.79	1.95	4
29. [Au(phen)Cl <sub>2</sub> ][AuCl <sub>4</sub> ]	2.11	2.74	4
30. Au(dmp)Cl <sub>3</sub>	0.65	—	4

TABLE II. Contributions (p.q.s.) of Some Ligands to the QS of Au(I) in ClAuN Complexes, with their Error Ranges. The contribution per ligand to the QS is 2 (p.q.s.). The ligands are ordered according to increasing  $\sigma$ -donor power.

Ligand	p.q.s. (mm/s)
Cl <sup>-</sup>	1.54(2)
NH(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	1.70(2)
N <sub>3</sub> <sup>-</sup>	1.71(2)
ino	1.71(4)
guo	1.65(10)
C <sub>5</sub> H <sub>5</sub> N	1.83(2)
pip	1.97(4)

It is very unlikely that these complexes have planar three coordination with  $sp^2(6s6p_z6p_y)$  hybridization [15]. Parish *et al.* [18] point out that the QS of three coordinated AuL<sub>3</sub> and two coordinated AuL<sub>2</sub> are expected to be nearly identical, whereas the IS decreases considerably on going from AuL<sub>2</sub> to AuL<sub>3</sub>, due to the increasing p-character of the Au—L bond, when the hybridization changes from sp to  $sp^2$  and due to the increasing bond length. When the formalism of Parish *et al.* [18] is used to calculate the QS values of three coordinate complexes from the experimental values of the appropriate two coordinate complexes, the agreement with the experimental IS and QS values is excellent [3]. Figure 3 for instance gives the experimental IS and QS values of the two coordinate complexes Au(PPh<sub>3</sub>)Cl and Au(PPh<sub>3</sub>)I [16]. The values for the three coordinated Au(PPh<sub>3</sub>)<sub>2</sub>Cl and Au(PPh<sub>3</sub>)<sub>2</sub>I are included [15]. The QS values of the latter two are slightly higher than those of the former ones, but their IS values are considerably less (1.4 mm/s). In Fig. 3 data of IS and QS, for known two coordinated AuL<sub>2-n</sub>Cl<sub>n</sub> (n = 0, 1, 2) complexes, (with L a nitrogen donor ligand), have been fitted to a straight line, according to

$$QS = 5.892 + 0.717 \times IS \quad (1)$$

The average environment rule describes quite well the bonding in the AuL<sub>2-n</sub>Cl<sub>n</sub> complexes. The QS values of (AuCl<sub>2</sub>)<sup>-</sup> and Au(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub><sup>+</sup> for instance yield a QS of 6.73 mm/s for Au(C<sub>5</sub>H<sub>5</sub>N)Cl via this rule, whereas the experimental value is 6.75 mm/s. The hypothetical three coordinated Au(C<sub>5</sub>H<sub>5</sub>N)Cl<sub>2</sub> should have a QS of 6.92 mm/s, according to the calculation method of Parish *et al.* [3]. However, the IS should be much less. Furthermore the Mössbauer parameters of the gold(I) nucleosides agree very well with eqn. 1. In view of the above considerations and the resemblance of the experi-

mental data of the Au(nucl)<sub>2</sub>Cl complexes with those of Au(C<sub>5</sub>H<sub>5</sub>N)Cl and AuNH(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>Cl, three coordination is very unlikely in the gold(I) nucleosides under consideration, while a N–Au–Cl coordination is more probable. The contributions to the QS of the ligands of different linear Cl–Au–N complexes have been ordered according to increasing covalency in Table II, including those of the nucleosides.

On the other hand the ir spectra are indicative of a Au–Cl bond in the Au(nucl)<sub>2</sub>Cl series because they show one band assigned to  $\nu$ Au–Cl at 330 cm<sup>-1</sup> [11], while the three coordinated Au(PPh<sub>3</sub>)<sub>2</sub>Cl [2] does not show any such band [15]. The <sup>1</sup>H nmr solution data show only one type of nucleoside signal, indicating that both nucleosides are coordinated to gold [11]. A rapid exchange of the nucleosides with solvent molecules is also possible in solution. It should be pointed out however that the Mössbauer evidence for an N–Au–Cl coordination in these complexes may be a result of their decomposition, both being very photosensitive. The Mössbauer spectrum of Au(ino)<sub>2</sub>Cl for example, demonstrates a partial disproportionation to metallic gold and the broad distribution in the spectrum of Au(guo)<sub>2</sub>Cl may be explained as the result of a decomposition, via a product with a possible N–Au–Cl coordination.

#### Gold(III) Complexes

The IS and QS values of the measured gold(III) complexes have been collected in Fig. 3 and Table I. All the Mössbauer parameters of complexes of the type AuL<sub>4-n</sub>Cl<sub>n</sub> (n = 0, 1, 2, 3, 4) (with L a nitrogen donor ligand) have been plotted in Fig. 3. The solid line represents a least squares fit of IS vs. QS of the complexes which are known to be square planar, resulting in the equation:

$$QS = -0.22 + 1.68 \times IS \quad (2)$$

The Au(III) nucleosides under study have been included in the fit, except for the Au(nucl – H<sup>+</sup>)Cl<sub>2</sub> compounds, which are coordinated also via O(6) or N(1) atoms besides N(7) and the [Au(nucl)<sub>2</sub>Cl<sub>2</sub>]Cl for which a different structure will be proposed. Eqn. 2 agrees reasonably well with the equation given by Viegers [12] for a collection of various types of square planar gold(III) complexes (QS = -0.22 + 1.74 × IS). The experimental IS and QS values of the gold(III) nucleosides included in the fit fall within the error ranges of the line of eqn. 2, supporting the assumption of a square planar configuration for these complexes.

#### The Au(nucl)Cl<sub>3</sub> series

The IS and QS of these complexes are considerably higher than those of the various AuCl<sub>4</sub><sup>-</sup> complexes (See Fig. 3). The latter complexes gave

QS values ranging from 0.75 mm/s for AuCl<sub>3</sub> [19] to 1.88 mm/s for (AsPh<sub>4</sub>)AuCl<sub>4</sub> [20]. The difference reflects the greater  $\sigma$ -donor strength of the nitrogen donor ligands, compared to the chlorine ligand. As in the gold(I) complexes, the guanosine ligand has higher  $\sigma$ -donor capacity than inosine, as is seen from the higher IS and QS values of the former. This also applies for the triacetyl derivatives. However, there is a decrease of about 0.5 mm/s in the QS values of the trino and trguo complexes (Figs. 2a and 2b). This difference cannot be explained only by the presence of the strongly electron withdrawing groups in the latter ligands, which are normally expected to decrease the electron density at N(7). A structural difference may also contribute to this phenomenon.

In order to discuss this structural difference it is useful to consider the Mössbauer hyperfine parameters derived from spectra of other gold(III) complexes with nitrogen donor ligands. The only other AuNCl<sub>3</sub> type complexes with known parameters are the (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>N<sub>2</sub>AuCl<sub>3</sub> [21] and C<sub>5</sub>H<sub>5</sub>NAuCl<sub>3</sub> [22]. Due to the poor resolution of the spectrum only the IS value of the latter compound could be determined. With the aid of eqn. 2 however, a QS value of 2.22 mm/s is obtained. The QS of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>N<sub>2</sub>AuCl<sub>3</sub> on the other hand amounts to 1.94 mm/s. Also the QS of (AsPh<sub>4</sub>)Au(N<sub>3</sub>)<sub>4</sub> is 2.92 mm/s [21].

The nitrogen donor ligands can be ordered according to their increasing  $\sigma$ -donor power, based on their p.q.s values. In square planar complexes with axial symmetry, the QS equals the sum of p.q.s values of the ligands [23]. The p.q.s of N<sub>3</sub><sup>-</sup> in the gold(III) complexes is 0.73 mm/s, as can be derived directly from the QS of (AuPh<sub>4</sub>)Au(N<sub>3</sub>)<sub>4</sub> [21]. The p.q.s of Cl<sup>-</sup> ranges from 0.14 mm/s in AuCl<sub>3</sub> to 0.47 mm/s in (AsPh<sub>4</sub>)AuCl<sub>4</sub>. In the series AuCl<sub>4</sub><sup>-</sup>, the IS and QS and therefore the p.q.s values appear to increase with increasing size of the cation [21]. Assuming equal p.q.s values of Cl<sup>-</sup> in the AuNCl<sub>3</sub> complexes under consideration, it can be concluded that the trino and trguo ligands gave similar p.q.s values to C<sub>5</sub>H<sub>5</sub>N since the QS values of Au(C<sub>5</sub>H<sub>5</sub>N)Cl<sub>3</sub> and Au(trino)Cl<sub>3</sub> and Au(trguo)Cl<sub>3</sub> are quite comparable (Table III and Fig. 3). Therefore Au(trino)Cl<sub>3</sub>, Au(trguo)Cl<sub>3</sub> and Au(C<sub>5</sub>H<sub>5</sub>N)Cl<sub>3</sub>, having comparable Mössbauer parameters, must have identical structures. The difference of 0.15 mm/s in the QS values of the trguo and trino complexes, is obviously due to the presence of the NH<sub>2</sub> group at C(2) in the former, which transfers electron density to the purine  $\pi$ -system and increases the basicity at N(7).

The difference of 0.41 mm/sec between the ino and trino complexes and 0.54 mm/sec between the guo and trguo complexes however, cannot be explained only by the presence of the acetyl groups in the triacetyl ligands but is also due to a slight structural

TABLE III. Contributions (p.q.s.) of Some Ligands and Donor-atoms to the QS of Au(III) in  $\text{AuCl}_n\text{L}_{4-n}$  Complexes, with Their Error Ranges. The p.q.s. values are derived in the text and ordered according to increasing  $\sigma$ -donor power.

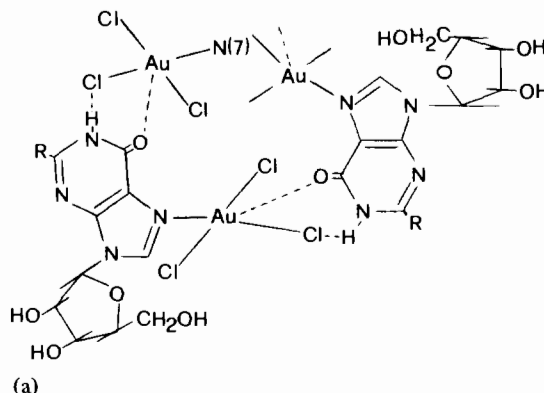
Ligand	p.q.s. (mm/s)
$(\text{C}_5\text{H}_5)_2\text{N}_2$	0.59(2)
$\text{N}_3^-$	0.73(2)
(tr)ino	0.76(5)
$\text{C}_5\text{H}_5\text{N}$	0.80(2)
tr(guo)	0.86(5)

difference between the two. It is logical to assume that the gold(III) ion, in the complexes  $\text{Au}(\text{ino})\text{Cl}_3$  and  $\text{Au}(\text{guo})\text{Cl}_3$  coordinates to more than one atom with a higher  $\sigma$ -donor capacity than the  $\text{Cl}^-$  ion. Since the N(7) is the one coordination site [11] and the N(1) and N(3) sites are excluded, the first bearing an imino proton and the second for steric reasons, the O(6) seems to be the second ligand site, which may weakly interact with Au(III), besides N(7). Although the ir spectra of  $\text{Au}(\text{ino})\text{Cl}_3$  and  $\text{Au}(\text{guo})\text{Cl}_3$  are not indicative of a strong Au–O bond, a weak interaction may well be postulated and this is consistent with the higher IS and QS values of these complexes compared with the values of the  $\text{Au}(\text{trino})\text{Cl}_3$  and  $\text{Au}(\text{trguo})\text{Cl}_3$  complexes. The ir spectra of the complexes [11] showed the  $\nu\text{C}=\text{O}$  at  $1680\text{ cm}^{-1}$  for the  $\text{Au}(\text{ino})\text{Cl}_3$  and at  $1690\text{ cm}^{-1}$  for the  $\text{Au}(\text{guo})\text{Cl}_3$ , a little lower than for the corresponding complexes with Pd(II), with no Pd–O interaction at all [24]. In the case of a strong metal oxygen interaction on the other hand, the  $\nu\text{C}=\text{O}$  was observed at  $1625\text{--}1630\text{ cm}^{-1}$ .

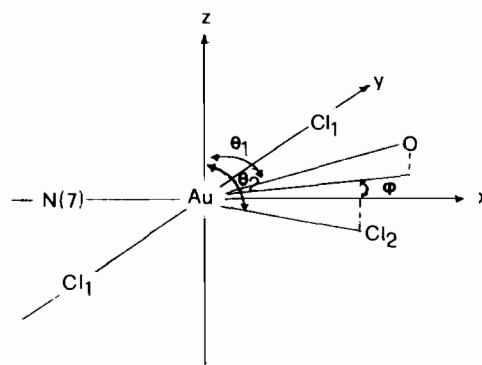
The weak Au(III)–O(6) interaction would result in a polymeric structure, as indicated schematically in Fig. 4a. The nearest Au–Cl bond may be somewhat distorted, with the  $\text{Cl}^-$  involved in hydrogen bonding with an N(1) imino proton. Figure 4b shows the corresponding positions of the atoms coordinated to gold(III). With the angle  $\phi = 0$ , this structure is nearly a trigonal bipyramidal one, intermediate in ligand exchange reactions of square planar complexes.

The QS of complexes with known structures without axial symmetry can be calculated, using the p.q.s. values of the ligands and the expressions for the elements of the electric field gradient (EFG) tensor, given by Bancroft [23] (See Appendix I).

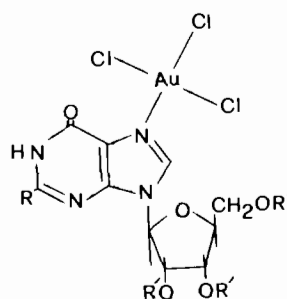
The model of a distorted five coordinate Au(III), with a weak Au–O interaction and one distorted Au–Cl bond, due to hydrogen bonding, explains the Mössbauer results fairly well, if these bonds make small angles with the X-axis,  $<30^\circ$  (Fig. 4).



(a)



(b)



(c)

Fig. 4. Proposed structures of  $\text{AuCl}_3(\text{nucl})$ . (a) Gold coordination in  $\text{Au}(\text{ino})\text{Cl}_3$  and  $\text{Au}(\text{guo})\text{Cl}_3$ , (b) The angles  $\theta_1$ ,  $\theta_2$  and  $\phi$  in a cartesian coordinate system and (c) Gold coordination in  $\text{Au}(\text{trino})\text{Cl}_3$  and  $\text{Au}(\text{trguo})\text{Cl}_3$ .

Similar results are obtained starting out with the experimental QS values of  $\text{Au}(\text{trguo})\text{Cl}_3$  and  $\text{Au}(\text{guo})\text{Cl}_3$ . For both pairs of nucleosides, the calculations yield reasonable results, only when the undistorted  $\text{Cl}^-$  ions lie in a *trans* position to each other. The corresponding model with *cis*  $\text{Cl}^-$  ions, yield to [O] values, is without physical meaning and should be rejected. The weak  $\sigma$ -donor capacity of the oxygen atom at C(6) is probably just enough reduced by the acetyl groups in the  $\text{Au}(\text{trino})\text{Cl}_3$

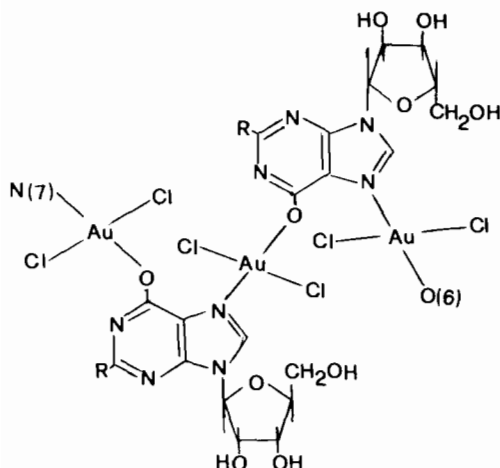


Fig. 5. Proposed structures of  $\text{AuCl}_2(\text{nucl} - \text{H}^+)$ . In  $\text{Au}(\text{trguo} - \text{H}^+)\text{Cl}_2$  and  $\text{Au}(\text{trino} - \text{H}^+)\text{Cl}_2$  the Au—O bond is longer than in  $\text{Au}(\text{guo} - \text{H}^+)\text{Cl}_2$  and  $\text{Au}(\text{ino} - \text{H}^+)\text{Cl}_2$ .

and  $\text{Au}(\text{trguo})\text{Cl}_3$ , to avoid any gold(III)—oxygen interaction in this series.

#### The $\text{Au}(\text{nucl} - \text{H}^+)\text{Cl}_2$ series

In this type of complex the ino and guo ligands follow the same order of increasing covalency as in the previous series; the  $\sigma$ -donor strength of the guo ligand is greater than that of the ino ligand. The  $\text{Au}(\text{nucl} - \text{H}^+)\text{Cl}_2$  coordinate through N(7) and O(6) or N(1) [11]. Assuming an O(6) coordination and taking into account that the Mössbauer parameters indicate square planar geometry and are higher than those of  $\text{Au}(\text{trino})\text{Cl}_3$  and  $\text{Au}(\text{trguo})\text{Cl}_3$ , the Au(III) environment in these complexes will be  $\text{AuNOCl}_2$ . For this structure and assuming the same p.q.s values for [N] and [Cl] as those of the  $\text{Au}(\text{nucl})\text{Cl}_3$  complexes, e.g.  $[\text{N}]_{\text{guo}} = 0.95$  mm/sec,  $[\text{N}]_{\text{ino}} = 0.86$  mm/s and  $[\text{Cl}] = 0.40$  mm/s, the p.q.s values of [O] in both complexes can be calculated (See Appendix). This calculation yields  $[\text{O}] = 1.10$  mm/s for the *cis* form and  $[\text{O}] = 0.84$  mm/s for the *trans* form in both complexes. Therefore these complexes must have a *trans* form, since the value of 0.84 mm/s is a reasonable p.q.s value for the oxygen donor atom (see also the previous section). The *trans* configuration is reasonable if the structure of Fig. 4a is correct, since the  $\text{Au}(\text{nucl} - \text{H}^+)\text{Cl}_2$  complexes are easily produced from the  $\text{Au}(\text{nucl})\text{Cl}_3$ , upon water dissolution [11]. In this way polymeric structures for the  $\text{Au}(\text{nucl} - \text{H}^+)\text{Cl}_2$  complexes are produced (See Fig. 5).

The IS and QS of  $\text{Au}(\text{trguo} - \text{H}^+)\text{Cl}_2$  are slightly lower than the IS and QS of  $\text{Au}(\text{guo} - \text{H}^+)\text{Cl}_2$ . Moreover, the ir spectrum of  $\text{Au}(\text{trguo} - \text{H}^+)\text{Cl}_2$  does not show considerable reduction of the  $\nu\text{C}=\text{O}$  frequency [11], indicating a weaker Au(III)—O<sup>-</sup>

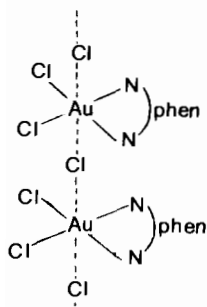
(6) interaction and a corresponding longer bonding distance in this case [11]. A longer Au—O bond is in agreement with the lower QS value. Substituting the QS of  $\text{Au}(\text{trguo} - \text{H}^+)\text{Cl}_2$  in eqn. 3 and using eqn. 7 and 9 of the Appendix a value of 0.73 mm/s for [O] is obtained. This corresponds to a longer Au—O bond by a factor of 1.05 in the  $\text{Au}(\text{trguo} - \text{H}^+)\text{Cl}_2$  compared to the  $\text{Au}(\text{guo} - \text{H}^+)\text{Cl}_2$  complex. This is related to the proposed structural difference between  $\text{Au}(\text{nucl})\text{Cl}_3$  with a weak Au—O interaction in  $\text{Au}(\text{ino})\text{Cl}_3$  and  $\text{Au}(\text{guo})\text{Cl}_3$  and no Au—O interaction at all in  $\text{Au}(\text{trino})\text{Cl}_3$  and  $\text{Au}(\text{trguo})\text{Cl}_3$ . This difference should be mainly due to the presence of the acetyl groups in the triacetyl derivative complexes. Finally, a Au—N(1) bonding cannot be excluded, although the Au—O(6) seems most likely.

#### The $[\text{Au}(\text{nucl})_2\text{Cl}_2]\text{Cl}$ series

The IS and QS values of these complexes are rather low, compared to those of  $\text{Au}(\text{trguo})\text{Cl}_3$  and  $\text{Au}(\text{trino})\text{Cl}_3$ , which are thought to have square planar  $\text{AuNCl}_3$  coordination. They are in fact, in the range of values measured for  $\text{AuCl}_4^-$  complexes (Fig. 3). However, it is very unlikely that the nucleosides are not directly coordinated to gold(III), in the  $[\text{Au}(\text{nucl})_2\text{Cl}_2]\text{Cl}$  complexes, as has been shown with <sup>1</sup>H nmr spectra [11]. Other explanations for the low IS and QS within the framework of a square planar geometry do not seem to be possible either.

Kateda *et al.* [4] reported on an interesting study of some mixed valence gold(I) and gold(III) complexes, which possess structures other than square planar in some cases. In their study, they reported, among others, on measurements of Au(III) (8-quinolinol) complexes, which coordinate through N(1) and the deprotonated O<sup>-</sup> group of C(8). The hyperfine parameters of  $\text{Au}(\text{oxine})\text{Cl}_2$  should therefore be comparable to those of  $\text{Au}(\text{guo} - \text{H}^+)_2$  and  $\text{Au}(\text{ino} - \text{H}^+)\text{Cl}_2$ . This is the case for the IS of the former, which is 1.73 mm/s. However, the QS is considerably less. The same phenomenon (a relatively low QS) is observed for  $\text{Au}(\text{oxine})_2^+$  in  $\text{Au}(\text{oxine})_2\text{AuCl}_4$ . Although a square planar geometry was proposed in both cases [4], the structures are probably somewhat distorted, since the IS and QS values deviate considerably from the line in the IS—QS plot, drawn with the data points of other square planar Au(III) complexes (Fig. 3).

The same authors [4] reported also on complexes of the type  $[\text{Au}(\text{III})(\text{phen})\text{Cl}_2]^+$  with various anions (phen = 1,10-phenanthroline), where the Au(III) coordinates through N(1) and N(10). In the Mössbauer spectrum of  $[\text{Au}(\text{phen})\text{Cl}_2]\text{Cl}$  the quadrupole splitting is not resolved and the IS is about 0.6 mm/s lower than the IS of other  $\text{AuN}_2\text{Cl}_2$  complexes. On the contrary, the Mössbauer parameters in  $[\text{Au}(\text{phen})\text{Cl}_2]\text{AuCl}_4$ , resemble more closely those of  $\text{AuN}_2\text{Cl}_2$  complexes, whereas the

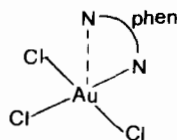
Fig. 6. Structure of  $[\text{AuCl}_2(\text{phen})]\text{Cl}$ .

parameters of  $[\text{Au}(\text{phen})\text{Cl}_2]\text{ClO}_4$  have intermediate values. Kateda *et al.* [4] proposed a structure for  $[\text{Au}(\text{phen})\text{Cl}_2]\text{Cl}$  in which the counterion  $\text{Cl}^-$  is situated between stacked  $[\text{Au}(\text{phen})\text{Cl}_2]^+$  bound to Au(III), in an approximately octahedral configuration elongated along the z-axis (Fig. 6). The similar  $[\text{Au}(2,9\text{-dimethyl-phen})\text{Cl}_2]\text{Cl}$  complex has been shown to have five-coordination [25] as illustrated in Fig. 7. The spectrum of this compound is also represented by an unresolved quadrupole doublet (small QS), with an IS even less than in  $[\text{Au}(\text{phen})\text{Cl}_2]\text{Cl}$ . Crystallographic data confirming this type of five coordination have been collected by Canty *et al.* [26] for  $\text{Au}(\text{CH}_3)_2(\text{tpzm})$ ,  $\text{Au}(\text{CH}_3)_2(\text{tpm})$  and  $\text{Au}(\text{CH}_3)_2(\text{dpt})$  in which tpzm, tpm and dpt represent tridentate nitrogen donor ligands.

The spectra of  $[\text{Au}(\text{nucl})_2\text{Cl}_2]\text{Cl}$  have similar characteristics to the above mentioned five- and six-coordinated complexes. Furthermore their IS values are comparable to those of  $[\text{Au}(\text{phen})\text{Cl}_2]\text{Cl}$ , whereas their QS values are less reduced. A similar structure to the one of  $[\text{Au}(\text{phen})\text{Cl}_2]\text{Cl}$  complex (Fig. 7) may also be proposed for the  $[\text{Au}(\text{nucl})_2\text{Cl}_2]\text{Cl}$  series. The smaller reduction of the QS here is probably caused by the length of the Au–Cl bond along the z-axis, which should therefore be longer than in  $[\text{Au}(\text{phen})\text{Cl}_2]\text{Cl}$ . The considerably large linewidth of the high velocity line in the  $[\text{Au}(\text{nucl})_2\text{Cl}_2]\text{Cl}$  spectra further reinforces the hypothesis of this polymeric structure, rather than five coordination, which is apparently more probable in the presence of bi- or tridentate ligands.

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Fig. 7. Structure of  $\text{Au}(\text{dmp})\text{Cl}_3$ .

### Appendix

#### Calculation of QS of the $\text{Au}(\text{nucl})\text{Cl}_3$ Series

For  $\text{Au}(\text{trino})\text{Cl}_3$  and  $\text{Au}(\text{trguo})\text{Cl}_3$  with square planar  $\text{AuNCl}_3$  coordination, the principal tensor elements  $V_{zz}$ ,  $V_{yy}$  and  $V_{xx}$  are given by:

$$\frac{V_{zz}}{e} = [3[\text{Cl}] + [\text{N}]] \quad (1)$$

$$n = \frac{V_{xx} - V_{yy}}{V_{zz}} = \frac{3[\text{N}] - 3[\text{Cl}]}{3[\text{Cl}] + [\text{N}]} \quad (2)$$

with

$$[\text{Cl}] = \frac{Z_{\text{Cl}}}{r_{\text{Au-Cl}}^3}$$

and

$$[\text{N}] = \frac{Z_{\text{N}}}{r_{\text{Au-N}}^3}$$

where  $Z$  is the effective nuclear charge and  $r$  the bonding distances of Au(III) to  $\text{Cl}^-$  and N, respectively.

With these tensor elements, the QS is calculated according to:

$$\text{QS} = eQV_{zz} \left( 1 + \frac{n^2}{3} \right)^{1/2} \quad (3)$$

where  $Q$  is the nuclear quadrupole moment of gold.

$[\text{Cl}^-]$  and  $[\text{N}]$  are usually expressed as partial quadrupole splittings, in units of  $\text{mm}/\text{sec}^{-1}$ , by multiplying by the constant  $e^2Q$ .

The expressions for the tensor elements of the EFG for  $\text{Au}(\text{ino})\text{Cl}_3$  and  $\text{Au}(\text{guo})\text{Cl}_3$  with the proposed structure shown in Fig. 4a, depend on the angles  $\phi$ ,  $\theta_1$  and  $\theta_2$  and the p.q.s values of  $[\text{Cl}^-]$ ,  $[\text{N}]$  and  $[\text{O}]$ . With the assumption that the distorted Au–Cl bonding distance is 10% longer than the other two, due to hydrogen bonding ( $r_{\text{Au-Cl}_2}/r_{\text{Au-Cl}_1} = 1.1$ ) the appropriate expressions (Fig. 4b) will be:

$$\begin{aligned} \frac{V_{zz}}{e} = & -[\text{N}] + (-2.75 + 2.75\cos^2\theta_2)[\text{Cl}_1] + \\ & + (3\cos^2\theta_1 - 1)[\text{O}] \end{aligned} \quad (4)$$



$$\frac{V_{xx} - V_{yy}}{e} = 3[N] + (-6 + 2.25 \sin^2 \theta_2)[Cl]_1 + 3 \sin^2 \theta_1 (\cos^2 \phi - \sin^2 \phi)[O] \quad (5)$$

Assuming that the direct effect of the acetyl groups on the  $\sigma$ -donor capacity of N(7) is rather small in Au(trino)Cl<sub>3</sub> and Au(trguo)Cl<sub>3</sub>, equal p.q.s values for [N] in both series of complexes may be postulated. With this approximation and a p.q.s of 0.40 mm/sec for the undistorted Cl<sup>-</sup> ligands in all complexes, the values of 0.86 mm/sec for the ino and trino complexes and of 0.95 mm/sec for the guo and trguo ones for the p.q.s of [N] are obtained. These are in agreement with the higher  $\sigma$ -donor power of the guo ligands.

The hypothesis of the distorted five coordinate structure of Au(ino)Cl<sub>3</sub> and Au(guo)Cl<sub>3</sub> outlined in Fig. 4, can now be checked, solving the set of eqns. 5, 6, 7 for [O], using the experimental QS values. The solution depends on the choice of the set of angles  $\phi$ ,  $\theta_1$  and  $\theta_2$ . Only those angle values which yield reasonable p.q.s for the [O] atom, are acceptable. The  $\sigma$ -donor capacity of oxygen is in general slightly less than that of nitrogen [12] and amounts to about 0.80 mm/sec for normal Au–O bonds, like in Au<sub>2</sub>O<sub>3</sub> [19]. For a weak Au–O interaction, [O] should be considerably reduced. In Fig. 8, a plot of calculated p.q.s values of [O] as functions of the angles  $\theta_1$ ,  $\theta_2$  and  $\phi$ , based on the experimental values of Au(trino)Cl<sub>3</sub> and Au(ino)Cl<sub>3</sub>, is given. Curve 1 gives [O] as a function of  $\theta_1$ , for  $\phi = 0^\circ$  and  $\theta_2 = 0$  yielding the lowest p.q.s values. Curves 2 and 3 with  $\phi = 0^\circ$  and  $\theta_2 = 105^\circ$  and  $120^\circ$  respectively, yield higher values for [O]. In the case of  $\phi \neq 0^\circ$ , e.g. the Au–O does not coincide with the X-axis (Fig. 4b), the calculated p.q.s values are higher than for  $\phi = 0^\circ$ .

It is well understood that solutions for [O] with a physical meaning should be less than 0.80 mm/sec, the p.q.s value of the O atom in a normal Au–O bond. For a weak Au–O interaction, this value is reduced proportional to the third power of the Au–O bond length:

$$\frac{[O]_1}{[O]_2} = \left( \frac{r_{Au-O_2}}{r_{Au-O_1}} \right)^3 \quad (6)$$

Using eqn. 6, the p.q.s of the [O] atom in weak Au–O interactions has been calculated as a function of  $r/r_0$ , the bond length in the complex, relative to the bond length in Au<sub>2</sub>O<sub>3</sub> and indicated in Fig. 4.

#### Calculation of the p.q.s of [O] in the Au(nucl – H<sup>+</sup>)Cl<sub>2</sub> Series

The EFG tensor elements are:

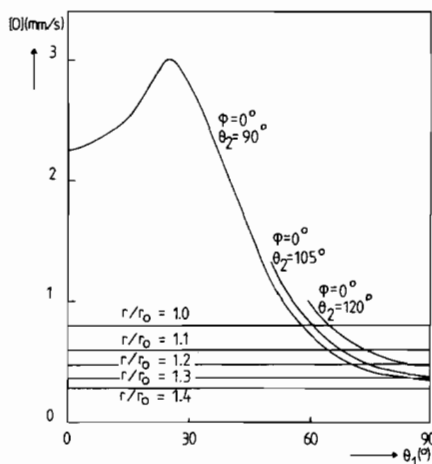


Fig. 8. The partial quadrupole splitting of the O-donor atom in Au(ino)Cl<sub>3</sub> calculated from the experimental quadrupole splitting with the coordination model indicated in Fig. 4b. [O] has been calculated for several values of the angles  $\theta_1$ ,  $\theta_2$  and  $\phi$ . The horizontal lines give [O] as a function of the Au–O bond length ( $r$ ) with respect to the Au–O bond length in Au<sub>2</sub>O<sub>3</sub> ( $r_0$ ).

$$\frac{V_{zz}}{e} = 2[Cl^-] + [N] + [O] \quad (7)$$

$$\text{cis form: } n = \frac{V_{xx} - V_{yy}}{V_{zz}} = \frac{3[O] - 3[N]}{2[Cl] + [N] + [O]} \quad (8)$$

$$\text{trans form: } n = \frac{V_{xx} - V_{yy}}{V_{zz}} = \frac{3[O] - 5[Cl] + 2[N]}{2[Cl] + [N] + [O]} \quad (9)$$

With [N]<sub>guo</sub> = 0.95 mm/s, [N]<sub>ino</sub> = 0.86 mm/s and [Cl] = 0.40 mm/s the calculation of the p.q.s of [O] for the cis form of the complexes can be made using eqn. 3, 7 and 8 and for the trans form, from 3, 7 and 9.

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