Chlorine-35 Quadrupole Resonance in Sodium Tetrachloroaurate(III) Dihydrate at High Pressure

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The ^{35}Cl quadrupole resonance in Na[AuCl$_4$]·2H$_2$O and its deuteriated derivative has been studied as a function of both temperature and pressure. Of the four crystallographically non-equivalent chlorine atoms, two show unique temperature and pressure coefficients; of these, one appears to be weakly hydrogen bonded to the water molecules, and the other is very probably the *trans* chlorine, the electronic effect being transmitted by a *trans* influence. The appreciable deuteriation shifts are temperature dependent and are attributed both to hydrogen-bond expansion and the effects of torsional oscillations of the water molecules. The high-pressure behaviour of the ^{35}Cl frequencies is explained in terms of a polarization of the non-bonding $3p_\pi$ electrons; under pressure, the local symmetry and electronic environment of three of the Cl atoms in the [AuCl$_4$]$^-$ ion cause the non-bonding electron clouds, principally $3p_z$ perpendicular to the [AuCl$_4$]$^-$ plane, to contract, which increases their quadrupole resonance frequencies, that of the fourth (the chlorine *trans* to the hydrogen-bonded atom) moving in the opposite direction, corresponding to an expansion of its $3p_z$ orbital. The relationship of these conclusions to the electronic mechanism of the *trans* influence is briefly discussed.

THE ^{35}Cl quadrupole resonance in sodium tetrachloroaurate(III) dihydrate has been studied by several workers.[1-3] The *X*-ray point symmetry[4] predicts four ^{35}Cl signals, as found experimentally,[2,3] but one of these shows a shift of *ca.* 2.5 MHz to low frequency and a positive tenperature coefficient. Similar effects are found in several isomorphous salts of the tetrachloroiodate(III)[5,6] and tetrahaloaurate(III) ions.[2,6] We have therefore investigated in more detail the effects of pressure and deuteriation on the ^{35}Cl frequencies in the hydrated sodium salt.

EXPERIMENTAL

Several samples of sodium tetrachloroaurate(III) dihydrate were examined, some purchased commercially and some prepared from metallic gold or AuCl$_3$.[7] The deuteriated samples were made by at least two recrystallizations from D$_2$O.

The ^{35}Cl frequencies were detected on a Decca n.q.r. spectrometer with sideband suppression and automatic frequency calibration, and a Bruker B-KR322s pulsed magnetic resonance spectrometer. The general features of the temperature dependence of the ^{35}Cl spectra have been reported previously,[2,3] and measurements on Na[AuCl$_4$]·2H$_2$O and Na[AuCl$_4$]·2D$_2$O were repeated in this work at fixed temperatures of 77, 195, and 273 K in order to measure the deuteriation shift more accurately. The high-pressure measurements were carried out in a beryllium–copper high-pressure vessel which has been described in more detail elsewhere;[8] frequency measurements were carried out at pressures up to 550 MPa, at both increasing and decreasing pressure, and in all cases the high-pressure vessel was thermostatted in a special Dewar. Temperature and pressure measurements are considered to be accurate to ±1.5 K and ±10 MPa respectively; the accuracy of the frequency measurements is ±5 kHz.

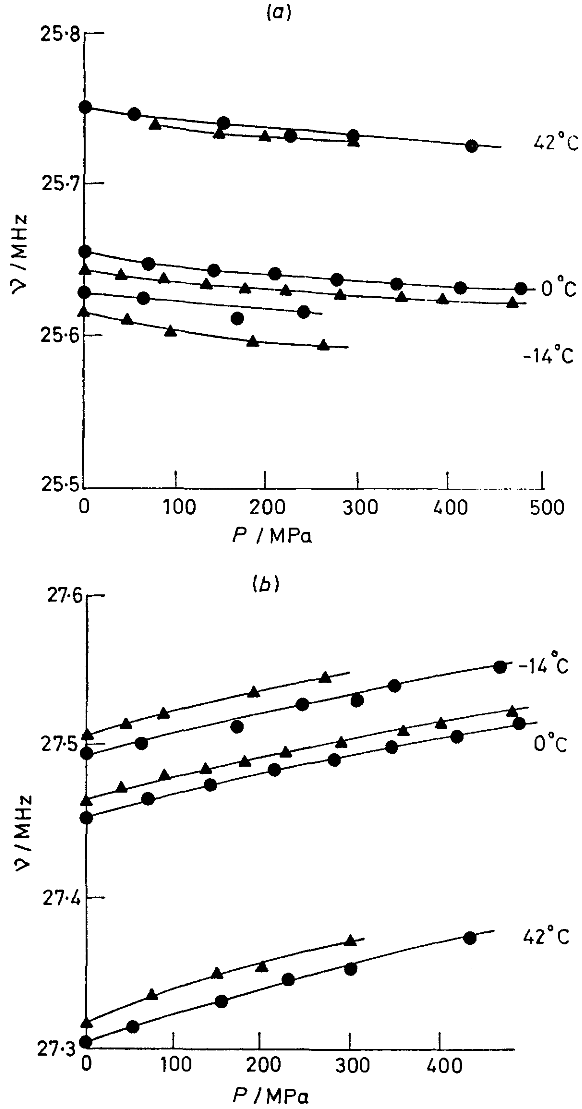
TABLE 1

Deuteriation shifts ($\nu_D - \nu_H$/kHz) for Na[AuCl$_4$]·2H$_2$O

		T/K					
		77		195		273	
	Line	ν_Q/MHz	$\delta = (\nu_D - \nu_H)$/kHz	ν_Q/MHz	$\delta = (\nu_D - \nu_H)$/kHz	ν_Q/MHz	$\delta = (\nu_D - \nu_H)$/kHz
D ν_D	H	29.453	+37	29.113	+8	28.832	−2
	D	29.490		29.121		28.830	
C ν_C	H	28.828	+100	28.628	+24	28.417	+10
	D	28.928		28.652		28.427	
B ν_B	H	27.981	+70	27.696	+17	27.453	+11
	D	28.051		27.713		27.464	
A ν_A	H	25.353	−110	25.500	−37	25.654	−6
	D	25.243		25.463		25.648	
Average frequencies	H	27.904		27.734		27.589	
	D	27.927		27.737		27.593	

RESULTS AND DISCUSSION

The deuteriation shifts for the four ^{35}Cl frequencies are given in Table 1 for Na[AuCl$_4$]·2H$_2$O at three different temperatures. As reported previously,[3] the lowest-frequency line, ν_A, shifts to lower frequency on deuteriation; the more accurate results for the other three lines, ν_B, ν_C, and ν_D, show that they shift to high frequency by varying extents. The temperature coefficients of lines ν_B and ν_D are very similar, and negative, whereas that of ν_A is positive and that of ν_C is negative but less so than ν_B and ν_D. Almost identical temperature behaviour has been observed [2,5] for ^{35}Cl or Br resonance in the isomorphous $Na[ICl_4]\cdot 2H_2O$ and $Na[AuBr_4]\cdot 2H_2O$. In other salts of these anions the patterns of behaviour are rather different and depend on the cation; [2] however, for $K[AuBr_4]\cdot 2H_2O$ there is a phase transition near 337 K in which lines defined as ν_A, ν_C and ν_B, ν_D at low temperatures come together to give a doublet ^{79}Br resonance at higher temperatures. The general conclusion seems to be that for $Na[AuCl_4]\cdot 2H_2O$ the signals are paired as far as their temperature behaviour is concerned: lines ν_A and ν_C show unusual behaviour, whereas that of ν_B and ν_D is similar and as expected.



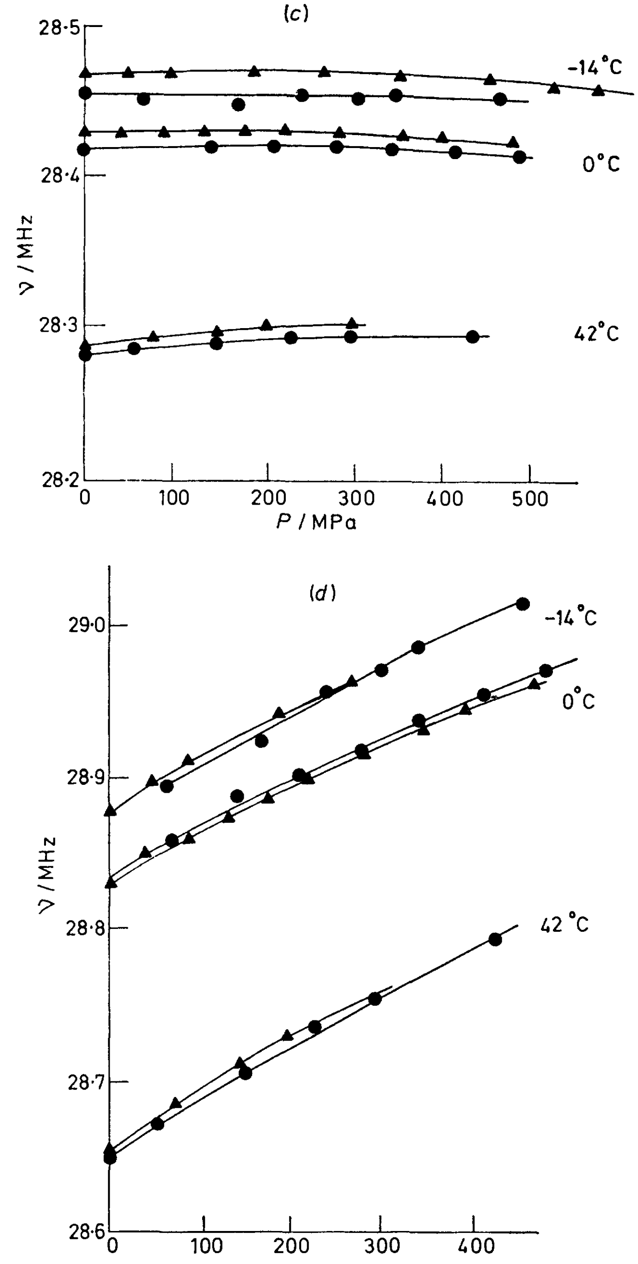


FIGURE 1 Pressure dependence of the ^{35}Cl quadrupole resonance frequencies in $Na[AuCl_4]\cdot 2H_2O$ (●) and $Na[AuCl_4]\cdot 2D_2O$ (▲) at three different temperatures: (*a*) ν_A, (*b*) ν_B, (*c*) ν_C, (*d*) ν_D

The same conclusions are derived from a study of the high-pressure data (Figure 1). Lines ν_B and ν_D show similar behaviour to that observed [9] in high-pressure studies of $K_2[PtCl_6]$, that is the frequency increases almost linearly with pressure, whereas lines ν_A and ν_C show small pressure dependences of opposite curvature. If $\nu = f(V,T)$, the pressure coefficients are related thermodynamically to the temperature coefficients by

$$\left(\frac{\partial\nu}{\partial T}\right)_P = -\frac{\alpha}{\chi}\left(\frac{\partial\nu}{\partial P}\right)_T + \left(\frac{\partial\nu}{\partial T}\right)_V \qquad (1)$$

equation (1) where α is the coefficient of cubic expansion and χ the volume compressibility (*without* signs). The second term on the right-hand side is expected to be small, so that all lines tend to show pressure and temperature coefficients of opposite sign.

It has been noted [6] that the average ^{35}Cl frequency of a number of tetrachloroaurates(III) is close to 27.8 MHz at 77 K and 27.3 MHz at room temperature, almost independent of the nature of the cation (although this does not appear to be true of the ^{197}Au quadrupole splitting observed in Mössbauer spectra [10]). In the series $K[AuCl_4]$, $Rb[AuCl_4]$, $Cs[AuCl_4]$, for example, the average ^{35}Cl frequencies (at 77 K) are 27.8, 28.0, and 28.1 MHz respectively.[2] This behaviour contrasts with that of the K^+, Rb^+, Cs^+, and other salts of $[SnCl_6]^{2-}$ and $[PtCl_6]^{2-}$, for which the ^{35}Cl frequency increases by more than twice as much, as the cubic unit cell expands with the larger cations.[11,12] Thus, in the series $K_2[PtCl_6]$, $Rb_2[PtCl_6]$, and $Cs_2[PtCl_6]$, the ^{35}Cl frequencies at 77 K are 26.0, 26.4, and 26.7 MHz. The Au–Cl stretching frequency (ν_1, A_{1g}) also shows little variation from that found in $[AuCl_4]^-$ ions in solution (348 cm^{-1}) to that in the Cs^+ (351) and $[NMe_4]^+$ salts (352),[13] whereas considerable cation effects are found for the Pt–Cl stretching frequency $\nu_1(A_{1g})$ in a series of hexachloroplatinates.[14–16]

Many $[ICl_4]^-$ and $[AuCl_4]^-$ salts are isomorphous,[2,5] in which case the ^{35}Cl frequency ratios of equivalent nuclei are remarkably constant except for ν_A, as Table 2(*a*) shows. Even when the tetrachloroaurate(III) is compared with the isomorphous tetrabromoaurate(III), the $^{79}Br/^{35}Cl$ ratios of the three higher frequencies are very similar in magnitude and lie close to those found in other isomorphous pairs [11,12] (*e.g.* 7.695 for $K_2[PtBr_6]$: $K_2[PtCl_6]$ and 7.764 for $Cs_2[PtBr_6]$: $Cs_2[PtCl_6]$) whereas the ν_A ratio is anomalously high.

TABLE 2

Chlorine-35 and $^{79}Br/^{35}Cl$ frequency ratios in some isomorphous salts

(*a*) $\dfrac{\nu(^{35}Cl)\ \text{in}\ Na[AuCl_4]\cdot 2H_2O}{\nu(^{35}Cl)\ \text{in}\ Na[ICl_4]\cdot 2H_2O}$

	77	193	293 K
ν_A	1.267	1.259	1.248
ν_B	1.236	1.236	1.238
ν_C	1.239	1.239	1.239
ν_D	1.232	1.232	1.236

(*b*) $\dfrac{\nu(^{79}Br)\ \text{in}\ Na[AuBr_4]\cdot 2H_2O}{\nu(^{35}Cl)\ \text{in}\ Na[AuCl_4]\cdot 2H_2O}$

	77	193	293 K
ν_A	7.955	7.947	7.947
ν_B	7.774	7.785	7.792
ν_C	7.776	7.781	7.790
ν_D	7.786	7.795	7.809

Many of these observations can be explained if we assume: first, that *one* of the chlorine atoms (Cl_A) in $Na[AuCl_4]\cdot 2H_2O$ is weakly hydrogen bonded to the water hydrogen atoms, and as a result its frequency is diminished by *ca.* 2.5 MHz; [2,3] and secondly, that this electronic effect is transmitted intramolecularly to the *trans* chlorine, Cl_C, by means of a *trans* influence.[6]

The evidence for hydrogen bonding from the crystal-structure analysis is not conclusive.[4] The hydrogen atoms are not located, but the oxygen atoms have close approaches (3.36—3.63 Å) to all four chlorine atoms of the planar $[AuCl_4]^-$ ion, the closest (two at 3.36 and two at 3.43 Å) being to Cl(1) with an Au–Cl · · · H–O angle of *ca.* 105°. If the hydrogen bonds are directed towards Cl(1) alone, the oxygen lone-pair electrons are also very favourably located with respect to the Na^+ ions.

The ^{17}O quadrupole coupling constant and asymmetry parameter [17] provide clear evidence for hydrogen bonding to oxygen; that the other partner in the bond is the chlorine atom of frequency ν_A is suggested first by its much lower frequency relative to the other chlorine nuclei and secondly by the deuteriation shifts, which are negative for $\nu_A (\nu_H > \nu_D)$ and positive for the remaining three frequencies ($\nu_H < \nu_D$), the ***mean*** frequencies remaining very similar. Negative deuteriation shifts have also been observed for ^{35}Cl resonance in $Na[ZnCl_4]\cdot 3H_2O$,[18] in which there is evidence for hydrogen bonding from ^2H magnetic resonance studies.[19] Although these shifts are small in comparison with those observed for ^{35}Cl quadrupole resonance in salts of the asymmetric dichloride ion,[20] in contrast they are strongly temperature dependent in $Na[AuCl_4]\cdot 2H_2O$, diminishing very considerably as the temperature is increased and becoming close to zero by 273 K.

In weak and asymmetric hydrogen bonds, deuteriation normally weakens the bond, *i.e.* the X–H · · · X distance expands slightly,[21] and this effect is apparently observed [22] in ^{127}I quadrupole-resonance studies of $[NEtH_3]I$ and $[NMeH_3]I$ and is claimed to be responsible for the large deuteriation shifts in the asymmetric $[HCl_2]^-$ ion.[20] In $Na[AuCl_4]\cdot 2H_2O$, however, although the ^{35}Cl frequency of ν_A shifts down by *ca.* 2.5 MHz with respect to the average value of 27.929 MHz at 77 K (Table 1), a shift which has been attributed to weak hydrogen bonding,[2,3] deuteriation produces a further downward shift, which is ***not*** consistent with the general behaviour of weak hydrogen bonds. We may explain this behaviour by assuming that the deuteriation shift ($\delta = \nu_D - \nu_H$) is the sum of two terms [equation (2)] of

$$\delta = \delta_0 + \delta_1 \tag{2}$$

opposite sign: δ_0, which is positive and little dependent on temperature, is usually the predominant term in strong but asymmetric hydrogen bonds and is due largely to the expansion in the hydrogen-bond length; [20] the second term, δ_1, which is negative, decreases very markedly with increasing temperature and is only comparable in magnitude with δ_0 in weak hydrogen bonds. δ_1 can be related to the difference in the mean-square torsional amplitudes of D_2O and H_2O molecules in the crystal.

For simple harmonic oscillations in a potential well of angular amplitude θ and at an angular frequency ω_t,[23] equation (3) is applicable where I_t is the molecular

$$\langle\theta^2\rangle = \frac{\hbar}{2I_t\omega_t}\left(\frac{1 + e^{-\hbar\omega_t/kT}}{1 - e^{-\hbar\omega_t/kT}}\right) \tag{3}$$

moment of inertia about the torsional axis. At low temperatures, the zero-point contribution is (4).

$$\langle\theta^2\rangle_0 = \hbar/2I_t\omega_t \tag{4}$$

The torsional frequencies have been detected in the neutron inelastic-scattering spectrum * and appear as a broad band near 320 cm^{-1} in $Na[AuCl_4]\cdot 2H_2O$. At

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* We are indebted to Dr. F. P. Temme for these measurements, performed on the 6 H spectrometer.

least three bands would have been expected, but are not apparently resolved. Assigning this frequency to torsional oscillations about the two-fold axis of the H_2O molecule, which has the lowest moment of inertia, we have (5) and hence calculate (6) and (7).

$$\frac{\langle\theta^2\rangle_0{}^{\mathrm{H}}}{\langle\theta^2\rangle_0{}^{\mathrm{D}}} = \frac{\omega_{\mathrm{t}}{}^{\mathrm{D}} I_{\mathrm{t}}{}^{\mathrm{D}}}{\omega_{\mathrm{t}}{}^{\mathrm{H}} I_{\mathrm{t}}{}^{\mathrm{H}}} = 2^{\frac{1}{2}} \tag{5}$$

$$\langle\theta^2\rangle_0{}^{\mathrm{H}} = 0.016\,5 \text{ rad}^2 \ (i.e.\ \langle\theta^2\rangle^{\frac{1}{2}} = 7{\cdot}4^\circ) \tag{6}$$

$$\langle\theta^2\rangle_0{}^{\mathrm{D}} = 0.011\,7 \text{ rad}^2 \tag{7}$$

The difference in mean-square torsional amplitude at any given temperature T may now be evaluated from equation (3), and values at three temperatures are given in Table 3 and compared with the deuteriation shifts taken from Table 1. The deuteriation shift δ is a linear function of $(\langle\theta^2\rangle^{\mathrm{H}} - \langle\theta^2\rangle^{\mathrm{D}})$, as in (8), of gradient -41.6 MHz rad^{-2} and intercept 81 kHz. A possible interpretation of this relation is as follows: as the temperature increases,

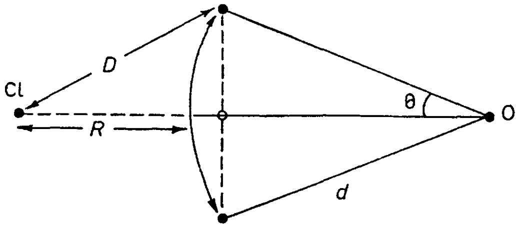

FIGURE 2 Effect of the torsional modes of the H_2O molecule on the average H · · · Cl distance

TABLE 3

Calculated mean-square torsional amplitudes of the water molecules in $Na[AuCl_4]{\cdot}2H_2O$ and $Na[AuCl_4]{\cdot}2D_2O$ compared with the experimental deuteriation shifts for ν_A

T/K	$\langle\theta^2\rangle^{\mathrm{H}}$	$\langle\theta^2\rangle^{\mathrm{D}}$	$(\langle\theta^2\rangle^{\mathrm{H}} - \langle\theta^2\rangle^{\mathrm{D}})$	δ/kHz
77	0.016 6	0.012 0	0.004 6	−110
195	0.019 9	0.017 1	0.002 8	−37
273	0.024 0	0.021 9	0.002 1	−6

$$\delta = \delta_0 + \delta_1 = \delta_0 + \delta'(\langle\theta^2\rangle^{\mathrm{H}} - \langle\theta^2\rangle^{\mathrm{D}}) \tag{8}$$

because the D_2O levels are closer spaced than those of H_2O and more occupied at higher temperature, the difference in the mean-square torsional amplitudes $(\langle\theta^2\rangle^{\mathrm{H}} - \langle\theta^2\rangle^{\mathrm{D}})$ diminishes, so that the intercept of 81 kHz represents the deuteriation shift δ_0 due to the expansion in the hydrogen bond. The origin of the second, temperature-dependent, term, δ_1, is more open to question. It has been attributed[8] to the slight contraction that should occur in the average H · · · Cl distance, D, when hydrogen is replaced by deuterium, as a result of the reduction in the mean-square torsional amplitudes. In Figure 2, for small torsional angles θ

$$\delta R = \langle D^2\rangle^{\frac{1}{2}} - R = d(R + d)\langle\theta^2\rangle/2R \tag{9}$$

and $R > d$, the contraction δR is found to be as in (9) and is therefore proportional to the mean-square amplitude $\langle\theta^2\rangle$. If the frequency shift is also proportional to this quantity, then the results in Table 3 are explained. The same mechanism should also make some contribution to the positive temperature dependence of ν_A which can be estimated from equation (3) and the value of the coefficient δ' taken from equation (8). Between 77 and 195 K, ν_A is predicted to increase by 137 kHz, compared to an experimental value of 47 kHz; between 195 and 273 K, the respective values are 170 and 154 kHz. At higher temperatures, therefore, the variation in amplitude of the H_2O torsional modes is sufficient to explain the temperature coefficient, but at <200 K other modes become of increasing importance, one of which is almost certainly the torsional oscillations of the $[AuCl_4]^-$ ion, which make a dominant contribution to the temperature dependence of ν_B and ν_D. Unfortunately, these modes could not be unambiguously assigned in the neutron inelastic-scattering spectrum.

The feeble nature of the hydrogen bonding in $Na[AuCl_4]{\cdot}2H_2O$ is shown by other evidence.* First, the shortest O · · · Cl approach (3.36 Å) is only slightly less than the sum of the O–H distance and H and Cl van der Waals radii (3.4 Å). Secondly, the ^{35}Cl frequency splittings in $[NH_4][AuCl_4]{\cdot}0.66H_2O$ are large, covering a range of 2.6 MHz at 160 K with the lower line showing a very low temperature coefficient,[2] and yet the hydrogen bonding is believed to involve the $[NH_4]^+$ and H_2O groups only;[24] despite the differences in ^{35}Cl frequency observed in this salt, the Au–Cl distances are almost identical, with a mean value of 2.26_8 Å, close to that found in[25] $[AsPh_4][AuCl_4]$ (2.271 Å) and the Na^+ salt (2.28 Å). The *d–d* and optical transitions in the planar $[AuCl_4]^-$ ion in $Na[AuCl_4]{\cdot}2H_2O$ have also been interpreted in terms of near tetragonal symmetry at the Au atom.[26] Nevertheless, the unusual behaviour of ν_A with respect to frequency shift and temperature coefficient has been observed[27] in the spectra of other hydrated chloro-complexes, *e.g.* $Ba[PtCl_6]{\cdot}6H_2O$, suggesting that the phenomenon is not confined to the $[AuCl_4]^-$ ion. In both these examples the charges on the chlorine atoms are nearly equal and of a magnitude (*ca.* 0.5e) consistent with weak and largely electrostatic hydrogen bonding. In $Na[AuCl_4]{\cdot}2H_2O$, the balance of evidence therefore supports the contention that the ^{35}Cl frequency shifts are accompanied by very little net change in the bonding electron distribution within the $[AuCl_4]^-$ ion, and that the origin of the observed effect should be sought in changes in the non-bonding $3p_\pi$ electrons on the chlorine atom, a model we have recently proposed to explain the high-pressure behaviour of the ^{35}Cl resonance in 1,3,5-trichlorobenzene[28] and some molecular complexes of 2,3,5,6-tetrachloro-*p*-benzoquinone.[29]

On this model, the $3p_\pi$ electrons are polarized by the intermolecular or interionic force field in a manner which is governed by the local symmetry; this polarization is represented by a change in the $3p_\pi$–$3d_\pi$ mixing, an increase in which will lower the contribution of the $3p_\pi$ electrons to the electric-field gradient along the bond axis (z) and hence lower the quadrupole coupling con-

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* *Note added in proof:* recent studies of the ^{1}H spin–lattice relaxation time (K. Sagisawa, H. Kitiyama, and R. Kitiyama, *Bull. Chem. Soc. Japan*, 1978, **51**, 1942) have shown that the H_2O molecules undergo hindered rotation about their C_2 axes with an activation energy of 26 kJ mol^{-1}.

stant.[28] In $Na[AuCl_4]\cdot 2H_2O$ the $[AuCl_4]^-$ ion lies in a plane of symmetry,[4] the average Au–Cl distance being 2.28 Å and Cl–Au–Cl angle 90.0°. The closed-shell d^8 configuration for Au means that the $3p_x$ orbitals on Cl (Figure 3) are unlikely to be involved in double bonding to the Au atom, and d_π–d_π interactions are also believed to be negligible.[30] This does not necessarily mean that η is zero, and indeed there is evidence from the Raman spectra that the two perpendicular bond-polarizability derivatives are unequal,[31] but it should be small and largely intermolecular in origin. Unlike the case of 1,3,5-trichlorobenzene, both the $3p_x$ and $3p_y$ orbitals on chlorine are non-bonding and therefore likely to be affected by compression of the crystal.

A parallel to the high-pressure behaviour of ν_B and ν_D occurs in $K_2[PtCl_6]$, $Rb_2[PtCl_6]$, and $Cs_2[PtCl_6]$ in which the ^{35}Cl frequency also increases almost linearly with pressure up to at least 400 MPa near 273 K.[9,32] The Pt–Cl bond in these crystals lies on a four-fold axis of symmetry [33] and there is little or no π bonding to be expected. The pressure constraints on the torsional modes of the $[PtCl_6]^{2-}$ ion will cause ν_Q to increase with pressure but it is reasonable to assume that $d\nu_{00}/dP$ is also positive [9] (ν_{00} being the ' rigid-lattice ' quadrupole resonance frequency, corrected for thermal motion), and we assume the same to be true for the two ^{35}Cl frequencies ν_B and ν_D in $Na[AuCl_4]\cdot 2H_2O$. The potassium, rubidium, and caesium hexachloroplatinates(IV) have a cubic structure, isomorphous with the corresponding hexachlorostannates(IV),[34] and the cation dependence of the ^{35}Cl frequency might be expected to show some parallels with the high-pressure behaviour of the bending and stretching frequencies of the anion as is observed for example in the i.r. and Raman spectra of the $[PtCl_6]^{2-}$ salts, where the order of pressure sensitivity [35,36] $\nu_1(A_{1g}) > \nu_2(E_g) > \nu_3(T_{1u})$ shows some relationship to that of the cation shift,[15,16,37] $\nu_1(A_{1g}) > \nu_2(E_g) \sim \nu_3(T_{1u})$. There is, however, a curious inconsistency in the ^{35}Cl quadrupole resonance results; whereas compression of $K_2[PtCl_6]$ increases the ^{35}Cl frequency,[32] expansion of the cubic lattice by the substitution of larger cations also has the *same* effect [12,34] in salts of both $[PtCl_6]^{2-}$ (at 23 °C) and $[SnCl_6]^{2-}$. In a series of solid solutions of $K_2[IrCl_6]$ and $K_2[PtCl_6]$, in which the cubic unit-cell dimension increases as the $[PtCl_6]^{2-}$ content decreases, the ^{35}Cl frequency of the latter shows a parallel increase.[38] Now the cation has no significant effect on the Pt–Cl [12,39] (or Sn–Cl [34]) distance, the usefulness of point charge models is a matter of dispute,[40,41] and after a careful summary of the arguments two groups of workers [11,41] have recently concluded that the cation shifts are dominated by ' covalency effects '. Brill [42] has suggested that a quenching of the Sternheimer antishielding factor by chlorine–chlorine repulsion in adjacent anions is responsible, the ^{35}Cl frequency decreasing as the Cl · · · Cl repulsions increase and showing good correlation with the Born repulsion term $e^{-r/\rho}$ (ρ being the ' hardness ' parameter). While it is agreed that the Cl · · · Cl contacts almost certainly have an effect on the Pt–Cl stretching frequency [hence the high pressure sensitivity [35,36] of $\nu_1(A_{1g})$] and also on the compressibility and lattice energy, the theory is still unable to account for the pressure shifts in the hexachloroplatinates(IV), and is moreover an unlikely model for covalent molecular ions with a relatively low charge on chlorine and low antishielding factor, as distinct from the alkali-metal halide ion pairs for which the theory was originally proposed. A polarization of the $3p_\pi$ charge cloud on the chlorine atom by anion–cation interelectronic repulsions is however able to explain much of the observed behaviour in both the hexachloroplatinates(IV) and tetrachloroaurates(III).

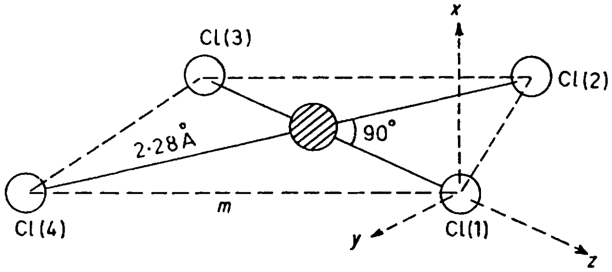

FIGURE 3 Axial system for the chlorine atoms in $[AuCl_4]^-$

The polarization of the non-bonding electrons is represented by a change in their $3d_\pi$ character λ, defined by equations (10) and (11). In axial symmetry, $\lambda_x = \lambda_y$

$$(p_x,d_{x^2-y^2}) = (1 + \lambda_x^2)^{-\frac{1}{2}}(p_x \pm \lambda_x d_{x^2-y^2}) \qquad (10)$$

$$(p_y,d_{xy}) = (1 + \lambda_y^2)^{-\frac{1}{2}}(p_y \pm \lambda_y d_{xy}) \qquad (11)$$

and the x and y axes become interchangeable. Similar equations can be written which involve the $3d_{zx}$ and $3d_{yz}$ orbitals on chlorine respectively and a discussion of which is the more likely mixing scheme is postponed until later. The effect on the contribution of the $3p_\pi$ electrons to the electric-field gradient $q_{zz}(q)$ along the Pt–Cl bond is (12), q_0 being the contribution of one $3p_z$

$$q = -2q_0(1 - \lambda^2) \qquad (12)$$

electron to q. Application of pressure compresses the non-bonding orbitals, corresponding to a decrease in λ and an increase in the quadrupole coupling constant and hence in the frequency (when η is small or zero). The origin of the compressive force is assumed to lie in the outer electrons of the cation, which under pressure approach and polarize the non-bonding orbitals of the chlorine atoms. The extent to which compression occurs may also depend on other factors, in particular the interanion Cl · · · Cl contacts;[11] however, the end-to-end approach of two chlorine atoms seems to have as little an effect on the quadrupole coupling constant as it does on the repulsion energies (see later).

In $K_2[PtCl_6]$, although the $K^+ \cdots$ Cl distance (3.45 Å) is larger than the sum of the ionic radii (3.14 Å), all the chlorine atoms have four close K^+ contacts and for each a non-zero overlap integral has been calculated,[34] so that polarization effects should be present; this conclusion is confirmed by the high pressure sensitivity[36] of the bending mode ν_4 (T_{1u}) and the lattice translation mode $\nu_L(T_{2g})$, the latter corresponding essentially to vibration of the K^+ ion against $[PtCl_6]^{2-}$. However, some care should be exercised in comparing n.q.r. spectra at high pressure, which are of necessity only seen under closely hydrostatic conditions, with i.r. and Raman data obtained from diamond anvil cells, where the pressure conditions are much less precisely defined. The sensitivity of the ^{35}Cl frequencies ν_B and ν_D in $Na[AuCl_4]\cdot 2H_2O$ to pressure is much greater than in $K_2[PtCl_6]$, the average values of $d\nu/dP$ near 273 K between 0 and 400 MPa being 0.121, 0.277, and 0.035 kHz MPa^{-1} respectively; this may partly originate in the closer $Na^+ \cdots Cl$ approaches, which are 3.18 Å to Cl(2) and 2.97 Å to Cl(4) (together with the greater polarizability of the chlorine $3p_x$ orbital in square-planar complexes), suggesting that ν_B should be assigned to Cl(2) and ν_D to Cl(4), in agreement with the order of frequencies.

An important distinction between the hexachloroplatinate(IV) salts and $Na[AuCl_4]\cdot 2H_2O$ should be emphasized, in that only the Pt–Cl bond possesses axial symmetry and has zero η. There is therefore no reason that λ_x and λ_y should be equal in the latter complex, nor need their pressure coefficients have even the same sign. The question could be resolved if the pressure dependence of η were known for each line, but in the absence of this information some tentative conclusions can be drawn from the present data. First, the high sensitivity to pressure of ν_D suggests that at least for this chlorine atom λ_x and λ_y both decrease with increasing pressure. Secondly, if ν_A is correctly assigned to Cl(1), then its large shift to low frequency is due to the approaches of hydrogen atoms lying above and below the $[AuCl_4]^-$ plane, which are expected to change λ_x more than λ_y. It could therefore be inferred that the $3p_x$ orbital in Figure 3 was more sensitive to intermolecular contacts than $3p_y$, and this is understandable in terms of polarization theory, since if contraction of a $3p_x$ orbital on one Cl atom is transmitted by a *trans*-influence into an expansion of the same orbital on a *trans* Cl atom there is nothing but the intermolecular and interionic forces to oppose this, whereas a similar mechanism for $3p_y$ would be resisted more strongly by the short intramolecular chlorine–chlorine contacts. Thirdly, the mirror plane in which the $[AuCl_4]^-$ ion lies prevents any anisotropic polarization of $3p_y$ [*i.e.* in equation (11) there is no distinction between the + and − sign] and it is plausible that the intramolecular $Cl \cdots Cl$ contacts would be a major factor in preventing any significant amount of lateral polarization, *i.e.* unidirectional distortion of the $3p_x$ electrons in directions parallel to the mirror plane, and they would certainly discourage any expansion of the $3p_y$ orbitals. An increase in either λ_x or λ_y with pressure is therefore unlikely.

The cation effects for the $[PtCl_6]^{2-}$ and $[SnCl_6]^{2-}$ ions originate in the increasing anion–cation repulsion as the cation increases in size, which leads to an increasing compression of the chlorine $3p_\pi$ orbitals and a decrease in λ. It is not unreasonable to suppose that this behaviour is possible *provided that* the anion is larger than the cation, so that the unit-cell dimension is determined largely by the interanionic chlorine–chlorine contacts, although it is in marked contrast to the decreasing anion–cation repulsion in the alkali-metal halides as the cation size increases.[43–45] There is, furthermore, other evidence: the chlorine–chlorine overlap integrals increase in the order $Cs_2[SnCl_6] > Rb_2[SnCl_6] > K_2[SnCl_6]$,[34] as do the total repulsion energies[44,45] and the predominant anion–cation contribution to these energies in the corresponding hexachloroplatinates(IV);[46] the optic lattice mode $\nu_L(T_{2g})$, which has a high sensitivity to pressure,[36] decreases from 88 cm^{-1} in $K_2[PtCl_6]$ to 70 cm^{-1} in $Cs_2[PtCl_6]$, but if the change in the reduced mass of the oscillators is taken into account,[47] the Hooke's law constant Λ actually increases, the ratio $\Lambda_{Cs^+}/\Lambda_{K^+}$ being 1.78; the rotary mode frequencies of $[PtCl_6]^{2-}$, which depend on the constant moment of inertia of this ion, are found to increase on going from the potassium to the caesium salt.[32] Although the $K^+ \cdots Cl^-$ distance in $K_2[PtCl_6]$ is 3.45 Å, larger than the sum of the ionic radii (3.14 Å), both the cation–chlorine and platinum–cation distances increase more slowly on going from $K_2[PtCl_6]$ to $Cs_2[PtCl_6]$ than the cation radii (the same is also true in the $[SnCl_6]^{2-}$ salts).

The changes in the $3p_\pi$ charge cloud are most unlikely to arise directly from the interatomic repulsion term. First, the changes in electron density produced by such repulsions are small except at distances of approach of less than half the van der Waals distance[48] and even then they are confined to regions remote from the nucleus. Secondly, the contributions of the $Cl \cdots Cl$ interactions to the total repulsion energy in the hexachloroplatinates(IV) are small.[45,46] Thirdly, the changes in the chlorine–cation overlap integral reported by Brill *et al.*[34] for the series $K_2[SnCl_6]$, $Rb_2[SnCl_6]$, and $Cs_2[SnCl_6]$ cannot account quantitatively for the cation shifts. An approximate equation for the change in the wavefunction ψ_C of a chlorine orbital under repulsion from a neighbouring atomic orbital ψ_M is (13) where S is the overlap

$$(\psi_C - S\psi_M)/(1 - S^2)^{\frac{1}{2}} \qquad (13)$$

integral. To a first approximation, the quadrupole coupling constants change in the ratio of $(1 - S^2)^{-1}$, so that on going from $K_2[SnCl_6]$ to the Rb^+ and Cs^+ salts the maximum predicted ratios $q(Rb^+)/q(K^+)$ and $q(Cs^+)/q(K^+)$ are 1.001 0 and 1.002 2 compared with experimental values of 1.036 and 1.065 at 296 K. This poor agreement would be little improved by any allowance for overlap charge density. The repulsion contributions are therefore much too small to account for the effects. On the other hand, the shift in quadrupole resonance frequency on going from $K_2[SnCl_6]$ to $Cs_2[SnCl_6]$ (1 MHz) corresponds to a change in λ^2 of *ca.* 0.01, which is reasonable compared to *d*-orbital populations found in calculations for other chlorine-containing molecules, *e.g.* 0.03 in HCl.[49]

Returning to a discussion of the other two ^{35}Cl frequencies in Na[AuCl$_4$]·2H$_2$O, we note that ν_C, which is now assigned to Cl(3), has similar intermolecular contacts to Cl(4), and should therefore have a similar pressure (and temperature) coefficient to ν_D; the difference could be explained by a *trans* influence due to the weak hydrogen bonding to Cl(1) (which has no close Na$^+$ approaches). *trans* Influences are known to be particularly effective in shifting ^{35}Cl quadrupole resonance frequencies,[3,50] and there is evidence from a force-constant analysis for their existence in the [AuCl$_4$]$^-$ ion.[13] The noteworthy feature of the present results is that the frequencies ν_A and ν_C shift in opposite directions with increase in pressure, the magnitude of the shift in ν_A being rather larger than that in ν_C, so that the mean frequency decreases; at >200 MPa, however, the pressure shifts show evidence of a change in sign, ν_A going through a minimum and ν_C through a maximum. It is particularly noticeable in the data at −14 °C for Na[AuCl$_4$]·2D$_2$O, where the maximum in ν_C and minimum in ν_A lie between 200 and 300 MPa, whereas in most other pressure plots the frequencies for the protonated and deuteriated forms run fairly parallel. It is therefore unlikely to be a change that affects the overall structure, and the most likely explanation is that the initial sign of dν/dP is due to the reduction in amplitude of the H$_2$O(D$_2$O) torsional modes, which strengthens the hydrogen bond and causes ν_A to decrease and ν_C to increase. The minimum in ν_A (and maximum in ν_C) occur when the electronic term becomes predominant, and the high-pressure evidence indicates that the $3p_\pi$ charge clouds for Cl(1) then begin to contract and those of Cl(3) to expand: on the $3p_\pi$ polarization theory, the positive sign of dν_A/dP at high pressure is attributed to decreasing d_π character in the non-bonding electrons as the $3p_\pi$ charge density moves closer on average to the Cl(1) nucleus, at the same time causing an expansion of the orbitals on the Cl(3) atom whose frequency therefore decreases. The fact that the minimum in ν_A and maximum in ν_C are first observed in the deuteriated form at −14 °C (the lowest temperature used in the high-pressure measurements) can be explained from equation (8). The lower the temperature the greater the importance of the second term on the right-hand side and provided that this is larger than δ_0 the average deuteron approach to the chlorine atom will always be closer than that of hydrogen and less compression is therefore required to change the sign of dν/dP.

Although the $3p_\pi$ polarization theory discussed in this paper has been concerned largely with changes in the nature of non-bonding orbitals in molecules, it may be of significance to other physical properties of crystals, such as the elastic constants and torsional frequencies, and is clearly of importance in understanding the electronic mechanism of the *trans* influence.[51] It is also worth noting that many of the unusual features of the temperature behaviour of the ^{35}Cl frequencies in Na[AuCl$_4$]·2H$_2$O have been observed in other tetrachloroaurate(III) salts,[2,6,52] *e.g.* [SCl$_3$][AuCl$_4$] and K[AuCl$_4$], in which there is no possibility of hydrogen bonding. The polarization forces that have been proposed are therefore of a general kind, and should be observed in other ionic crystals, such as salts of [PbCl$_6$]$^{2-}$, [ReCl$_6$]$^{2-}$, and [TeCl$_6$]$^{2-}$ which show similar cation effects[11] to those of [SnCl$_6$]$^{2-}$, and the alkali-metal salts of [PdCl$_4$]$^{2-}$ and [PtCl$_4$]$^{2-}$ for which very few frequencies are at present available.[3,53]

In conclusion, we note that the discussion of the polarization model has been conducted without specific reference to the *d* orbitals involved, although it is implied that p_x–$d_{x^2-y^2}$ mixing occurs, as we have assumed in treating the high-pressure behaviour of aromatic C–Cl bonds,[28] and that the d_{zx} orbitals may also play a role. If, however, there is no significant π bonding in the M–Cl bond, it is possible that p_x–d_{zx} mixing could contribute very significantly to the distortion of the chlorine $3p_\pi$ orbitals, in which case the model bears a close relationship to the p_π–d_π polarization theory proposed for the *trans* effect.[51] In this model, under the influence of an approaching ligand, the p_π and d_π orbitals of one Cl atom are hybridized to form a *pd* hybrid orbital, the lobes of which are directed toward the Pt atom. In Figure 4 this is illustrated diagrammatically, the chlorine electrons being represented by a d_π orbital. The Pt d_π orbital is thereby polarized, and the effect is transmitted directly to the *trans*-ligand orbitals. Within the complex ion, it is believed that 'the displacement of the Pt charge density is due more to the Pauli exclusion principle than to the electrostatic field',[51] which means that it is a short-range effect hardly likely to be affected by the relatively low pressures used in these experiments. However, external fields might still influence the chlorine charge density by the mechanism illustrated in an exaggerated form in Figure 4; the weak hydrogen bonding to Cl(1), for example, could expand the p_π–d_π hybrid orbital on that chlorine by increasing the degree of mixing, an effect which is then transmitted by the polarization mechanism to the *trans*-chlorine ligand, Cl(3), whose p_π–d_π hybrid orbital contracts. There would be slight adjustments to the charge density at Au (which might be responsible for the cation effect observed in the ^{197}Au Mössbauer spectra[10]) but the changes in the gold–chlorine interactions would largely compensate each other, so that the intramolecular

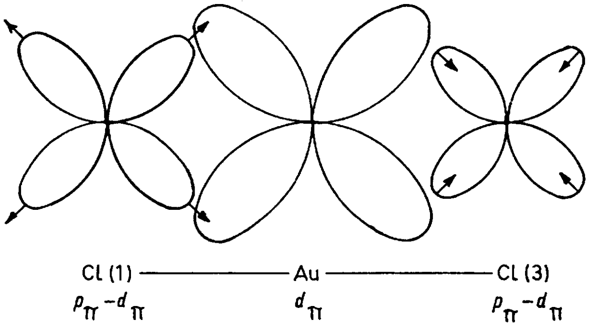

FIGURE 4 Polarization model of the *trans* effect

bonding energy remained unaffected. The net effect would be to raise the Cl(3) frequency by almost as much as the Cl(1) frequency is lowered, as is observed in the pressure dependence. Hence the insensitivity of the average ^{35}Cl frequency in the $[AuCl_4]^-$ anion to the nature of the cation; the shifts that are observed could be explained by the much smaller distortion of the $3p_y$ orbitals. In ions with octahedral symmetry, however, the $3p_x$ and $3p_y$ chlorine orbitals are equivalent and their expansion is equally resisted by their four nearest intramolecular neighbours and nearest cations; symmetry therefore forbids the expansion of one set of chlorine orbitals at the expense of the contraction of another, so that under pressure *all* the non-bonding orbitals contract and the frequency increases.

Further high-pressure studies are planned to check these tentative conclusions.

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