Static and Dynamic Structure of Au_2Cl_6, $AuAlCl_6$ and $AuFeCl_6$ Clusters

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Fourfold coordination of trivalent metal ions by chlorines in molecular dimers changes from tetrahedral in Al_2Cl_6 and Fe_2Cl_6 to planar in Au_2Cl_6. Within an ionic model we interpret this transition in the stable molecular shape as due to the quadrupolar polarizability of the gold(III) ion. We also demonstrate within the same model that a mixed tetrahedral-planar coordination is stable in $AuAlCl_6$ and $AuFeCl_6$ clusters. Quantitative comparisons are presented for the calculated molecular structures and vibrational frequencies against the available experimental data from crystalline diffraction and from Raman spectra of the crystal and of vapours.

Key words: Ionic Clusters; Molecular Vapours; Molecular Crystals.

1. Introduction

The crystal structure of gold(III) chloride as determined by Clark *et al.* [1] can be viewed as formed from lattice cells containing pairs of planar Au_2Cl_6 molecules and arranged in a monoclinic ordering. Inside one of these molecules, each gold ion is coordinated by two bridging and two terminal chlorines lying at the corners of a slightly deformed square. Nalbandian and Papatheodorou [2] measured the Raman spectra of this solid compound and performed a normal mode analysis of the measured spectrum on the basis of the known crystal structure, obtaining a complete force field. They further showed that this force field yields agreement with some measured Raman modes both for the Au_2Cl_6 molecule in the vapour and for the $AuAlCl_6$ vapour complex, the latter being formed as a minority species in Al_2Cl_6 vapours over solid gold(III) chloride [3]. In their analysis they assumed for the $AuAlCl_6$ molecule a structure which is intermediate between the tetrahedral coordination existing in the Al_2Cl_6 molecule [4] and the square-type coordination in Au_2Cl_6.

While a tetrahedral-type coordination by halogens is quite common for trivalent-metal ions in low-density (liquid and vapour) states [5], the planar structure of Au_2Cl_6 is very striking and apparently as yet not accounted for in a theoretical model. If for simplicity we contrast these two types of coordination in the $AlCl_4$ and $AuCl_4$ molecular-ion monomers, we may view the $AuCl_4$ square as arising from the $AlCl_4$ tetrahedron under lowering of three-dimensional rotational symmetry. From this viewpoint there should be little doubt that the main driving force for such symmetry breaking is the high quadrupolar polarizability of the gold(III) ion.

In the present work we evaluate the equilibrium structures and the vibrational spectra of the Au_2Cl_6, $AuAlCl_6$, and $AuFeCl_6$ molecules by means of a microscopic ionic model. We start from our earlier studies of Al_2Cl_6-based clusters [6] and of the Fe_2Cl_6 and $AlFeCl_6$ molecules [7] and augment them by inclusion of the interactions between ionic charges and induced quadrupoles. The model includes as free parameters the ionic radius and the quadrupole polarizability of gold(III). Through a sensible estimation of these parameters, we can assess the equilibrium structures of the three molecules of present interest and obtain a rather good overall account of the available experimental evidence.

2. Interionic Force Model

In our earlier studies of trivalent-metal chlorides [6, 7] we constructed an expression for the potential energy $U(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\})$ of an ionic cluster as a function of the interionic bond vectors $\boldsymbol{r}_{ij}$ and of the electric dipole moments $\boldsymbol{p}_i$.This was based on a suitable extension of the shell model (also known as the deformation dipole model) for the lattice dynamics of ionic

Table 1. Interionic force parameters in Au_2Cl_6.

	z_{Au}	z_{Cl}	R_{Au} (Å)	ρ_{Au} (Å)	R_{Cl} (Å)	ρ_{Cl} (Å)	C_{Cl} (eÅ$^{5/2}$)	α_{Cl} (Å^3)	α_{s} (Å^3/e)	Q_{Au} (e^{2}Å^5)
Al-like	2.47_2	$-.82_4$	1.16	0.054	1.71	0.238	5.5	2.05	0.46	9.5
Fe-like	2.30_4	$-.76_8$	1.13	0.049	1.71	0.238	5.5	2.72	0.66	9.5

and semiconductor crystals [8]. A basic quantum mechanical justification for this approach to molecular structure has been given for alkali halides by means of exchange perturbation theory [9, 10]. For the detailed expressions entering $U(\{\boldsymbol{r}_{ij}\},\{\boldsymbol{p}_i\})$ we refer to our earlier work [6].

In dealing with gold(III)-based chlorides we extend the exchange perturbation approach to include the induction of a quadrupolar moment on gold(III) by the ionic charges in the molecule. The relevant quantity is, of course, the electric field gradient $E_{\alpha\beta}$. Considering first an $AuCl_4$ molecular ion, we write

$$E_{\alpha\beta} = \sum_{i=1}^{4} \left[-3\frac{R_{i\alpha}R_{i\beta}}{R_i^5} + \frac{1}{R_i^3}\delta_{\alpha\beta} \right], \tag{1}$$

where $\boldsymbol{R}_i$ is the vector joining Au to the i-th Cl and a Greek suffix denotes a Cartesian component. The interaction energy with the quadrupolar moment $Q_{\alpha\beta}$ on Au thus is

$$U_Q = \sum_{\alpha,\beta} Q_{\alpha\beta}E_{\alpha\beta}. \tag{2}$$

Since the quadrupole moment $Q_{\alpha\beta}$ is in fact induced by the electric field gradient, we have for a planar-molecule (lying in the (x, y) plane, say) the result

$$U_Q = -Q\sum_{i=1}^{4} \frac{R_{ix}^4 + R_{iy}^4}{R_i^{10}}, \tag{3}$$

where Q is a constant measuring the quadrupolar polarizability of gold(III). We have obtained a first estimate of this quantity by starting from a (stable) tetrahedral shape for $AuCl_4$ at $Q = 0$ and by increasing Q until the stable shape has become a square.

For a full assessment of the model parameters describing the gold-based chloride clusters, we have assumed transferability of a number of parameters between different systems as in our earlier studies and adjusted the quadrupolar parameter Q_{Au} and the ionic radius R_{Au} to the known structure of the Au_2Cl_6 molecule in the gold trichloride crystal [1]. The transferred parameters are (i) the effective valences z_{Cl} and $z_{\mathrm{Au}} = -3z_{\mathrm{Cl}}$, (ii) the electric dipole polarizability α_{Cl}, the short-range polarizability α_{s} and the van der Waals coefficient C_{Cl} for the chlorines, (iii) the ionic radius R_{Cl} and the stiffness parameter ρ_{Cl} describing the contribution of the chlorines in the Busing form [11] of the Au-Cl overlap repulsions, and (iv) the ratio $R_{\mathrm{Au}}/\rho_{\mathrm{Au}}$ of the analogous quantities for gold(III). We have tested the reliability of this transfer by evaluating two alternative choices of these parameters, *i. e.* their values obtained in our earlier studies of Al_2Cl_6 [6] and of Fe_2Cl_6 [7]. In the followingwe refer to these two choices as “Al-like” and “Fe-like”.

Table 1 shows the two alternative sets of model parameters that we have used in the calculations reported in the sequel. Of course, in dealing with $AuAlCl_6$ and with $AuFeCl_6$ we have used the Al-like and Fe-like sets of parameters, respectively.

3. Equilibrium Structures

The calculated equilibrium shape of the Au_2Cl_6 molecule is shown in Figure 1. Table 2 reports the values of its structural parameters, in comparison with the data on Au_2Cl_6 molecules in gold trichloride crystals from the experiments of Clark *et al.* [1]. The symbols Cl^T and Cl^B denote a terminal and a bonding chlorine, respectively.

It is evident from Table 2 that there is substantial agreement between the results obtained with the

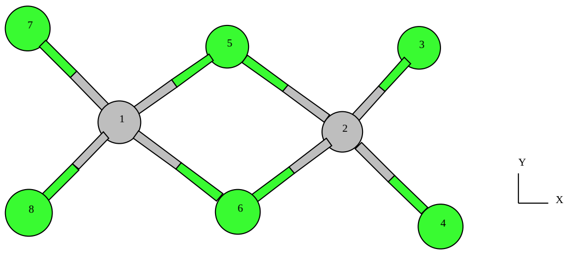

Fig. 1. A ball-and-stick model of the structure of the Au_2Cl_6 molecule, showing the two gold(III) ions in a distorted square coordination by chlorines.

Table 2. Equilibrium structure of Au_2Cl_6 (bond lengths in Å, bond angles indegrees).

	Au-Cl^T	Au-Cl^B	Au-Au	∠ Cl^T-Au-Cl^T	∠ Cl^B-Au-Cl^B
Al-like	2.21	2.36	3.61	99.4	80.4
Fe-like	2.24	2.37	3.53	98.5	83.7
Crystal [1]	2.24	2.33	3.41	90.0	86.0

Table 3. Equilibrium structure of $AuAlCl_6$ and $AuFeCl_6$ (first and third row), in comparison with those of M_2Cl_6 and Au_2Cl_6 for M = Al (second row) and M = Fe (fourth row).

M-Cl^T	M-Cl^B	Au-Cl^T	Au-Cl^B	∠Cl^T-M-Cl^T	∠Cl^B-M-Cl^B	∠Cl^T-Au-Cl^T	∠Cl^B-Au-Cl^B
2.07	2.25	2.21	2.37	121	88	99	82
2.06	2.28	2.21	2.36	121	90	99	80
2.16	2.31	2.24	2.38	120	90	98	87
2.15	2.33	2.24	2.37	120	94	98	84

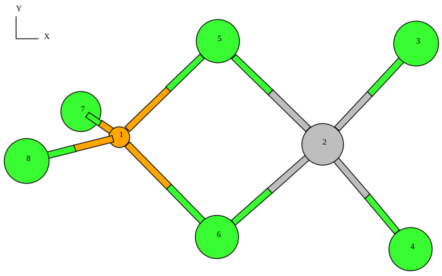

Fig. 2. A ball-and-stick model of the structure of the $AuAlCl_6$ and $AuFeCl_6$ molecules, showing the gold(III) ion in a distorted square coordination and the other trivalent metal ion in a distorted tetrahedral coordination.

two alternative sets of model parameters, both sets of results being in very reasonable agreement with the crystal diffraction data.

Figure 2 shows the calculated equilibrium shape of the $AuAlCl_6$ molecule. As proposed by Nalbandian and Papatheodorou [2], it can be viewed as obtained from matching the tetrahedral structure of $AlCl_4$ with a square structure for $AuCl_4$ through bridging by a pair of chlorines. The quantitative extent to which this is true is shown in Table 3 by reporting the structural parameters of $AuAlCl_6$ in comparison with those of Al_2Cl_6 [6] and of Au_2Cl_6 (see Table 2). Evidently, it is an excellent approximation to take the values of bond lengths and bond angles in the mixed molecule from the parent dimers. We obtain qualitatively similar results for the $AuFeCl_6$ molecule (see Table 3).

In concluding this section we remark that from our calculations we find that the induced-quadrupole contribution to the binding energy of these molecules is quite appreciable, of the order of 3.6 - 3.9 eV per gold ion. In spite of this we find that both mixed molecules are somewhat more strongly bound than the Au_2Cl_6 one, by about 2 eV in the case of $AuAlCl_6$ and by almost 1 eV in the case of $AuFeCl_6$.

Table 4. Frequencies of vibrational modes for Au_2Cl_6 (in cm^{-1}).

		Au_2Cl_6-calc. Al-like	Au_2Cl_6-calc. Fe-like	Au_2Cl_6-meas. [2] Crystal	Au_2Cl_6-meas. [2] Vapour
A_g	ν_1	376	360	378	386
	ν_2	327	325	327	324
	ν_3	166	158	166	157
	ν_4	103	103	97	96
A_u	ν_5	89	86	–	–
B_{1g}	ν_6	364	350	365	–
	ν_7	237	238	288	–
	ν_8	135	129	122	–
B_{1u}	ν_9	161	153	135	–
	ν_{10}	73	69	–	–
B_{2g}	ν_{11}	115	109	104	–
B_{2u}	ν_{12}	382	365	383	–
	ν_{13}	283	280	313	–
	ν_{14}	100	95	80	–
B_{3g}	ν_{15}	112	107	–	–
B_{3u}	ν_{16}	365	350	373	–
	ν_{17}	278	279	309	–
	ν_{18}	165	157	143	–

4. Vibrational Frequencies

The calculated vibrational frequencies of the molecules whose structure we have evaluated in Sect. 3 are reported in Tables 4 and 5. Table 4 compares our results for the Au_2Cl_6 molecule with the Raman scattering data of Nalbandian and Papatheodorou [2] on both the gold trichloride crystal and the gaseous molecule. In Table 5 we give our results for the mixed $AuFeCl_6$ and $AuAlCl_6$ molecules, together with the values measured by the same authors for the latter molecule. We do not consider fits of the experimental data by the valence force field method.

The agreement between calculated and measured spectra in Tables 4 and 5 can be considered as very reasonable, considering that the calculations have been carried out within a microscopic model of the full molecular potential energy and that none of these data has been fitted in the adjustment of the model parameters. The agreement is quite good for the bond-stretching modes at high frequency, but appears to be somewhat less satisfactory as one moves into the region of bond-bending modes. Again, there is substantial agreement between the results reported for Au_2Cl_6 in Table 4 as obtained from our two alternative sets of model parameters.

5. Concluding Remarks

We have in this work described a microscopic model of ionic interactions in gold-based trichlorides, including contributions to the potential energy from induced quadrupoles on the gold(III) ion. Through these contributions we have been able to account for the planar structure of the Au_2Cl_6 molecule and to demonstrate the coexistence of distorted tetrahedral and square coordinations in the $AuAlCl_6$ and $AuFeCl_6$ molecules.

The reasonably accurate description of structural data and vibrational frequencies that we have achieved with the help of a minimal number of free parameters validates the model and suggests that it should find useful applications in further studies of condensed states of these materials.

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Table 5. Frequencies of vibrational modes for $AuFeCl_6$ and $AuAlCl_6$ (in cm^{-1}).

		$AuFeCl_6$ - calc.	$AuAlCl_6$ -calc.	$AuAlCl_6$ - meas. [2]
A_1	ν_1	411	507	495
	ν_2	350	380	386
	ν_3	325	358	(330)
	ν_4	270	284	300
	ν_5	161	191	183
	ν_6	122	140	156
	ν_7	90	97	(98)
A_2	ν_8	107	113	–
	ν_9	68	73	–
B_1	ν_{10}	460	616	–
	ν_{11}	151	170	–
	ν_{12}	112	133	–
	ν_{13}	56	60	–
B_2	ν_{14}	363	382	–
	ν_{15}	341	360	–
	ν_{16}	219	220	–
	ν_{17}	151	162	–
	ν_{18}	87	94	–

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