Single-crystal and Solution Near-ultraviolet–Visible Spectra of Sodium Tetrachloroaurate

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Temperature-dependent and polarised electronic spectra of a single crystal of sodium tetrachloroaurate dihydrate are reported and the ${}^1A_{1g}\rightarrow{}^1A_{2g}(d_{xy}\rightarrow d_{x^2-y^2})$, ${}^1A_{1g}\rightarrow{}^1B_{2g}(d_{xy}\rightarrow s)$, and ${}^1A_{1g}\rightarrow{}^1E_g(d_{xy}\rightarrow d_{xz}d_{yz})$ transitions assigned.

THE tetrachloroaurate ion and its substituted derivatives are often used as starting materials in studies of gold-solution chemistry, and their near-u.v.–visible spectra provide a simple method of monitoring the facile valence state and co-ordination changes they undergo. The spectra are by no means understood. For example, apart from some differences in intensity, the ion $[AuCl_3OH]^-$ has a very similar spectrum to that of $[AuCl_4]^-$,[1] in spite of the fact that both the geometry and electron-density distribution round the gold atom have been changed. We have found the same effect with a monosubstituted sulphur complex, $AuCl_3[SCH\cdot CO_2H\cdot CH_2\cdot CO_2H]^-$ (ref. 2) and it has also been reported for the species $AuCl_3\cdot Me_2SO$.[3] To facilitate our studies of the use of gold complexes in the treatment of rheumatoid arthritis, we required a better understanding of the spectra of gold(III). As part of a study of the problem, we now report the results of a study of the single-crystal spectrum of sodium tetrachloroaurate dihydrate.

EXPERIMENTAL

Sodium tetrachloroaurate dihydrate crystals were grown from solution as well-defined rhombs and two of these were oriented by use of precession and Weissenberg *X*-ray methods. The orthorhombic crystals, space group *Pnma*,[4] have the *b* axis along the longest direction of the rhomb. Under the optical microscope the crystals are dichroic, being colourless with polarised light propagated along the *b* axis and yellow with light propagated along the *a* or *c* axis. Sections with the *a* and *c* axes in the plane were yellow and showed no appreciable dichroism. The compound reacts with many organic compounds, such as wax, grease, and polishing fluids and we therefore had some difficulty in polishing the soft crystals down to sufficiently thin sections for spectroscopic work. Thin crystals grown *in situ* on silica plates proved much more suitable and were used in the spectral studies. They have a similar morphology to those described, and both the morphology and dichroism indicate that the face studied contains the *b* axis.

Spectra were taken by use of a Displex closed-cycle refrigerator system with a temperature range of 10—300 K and a Pye Unicam SP 1800 spectrometer.

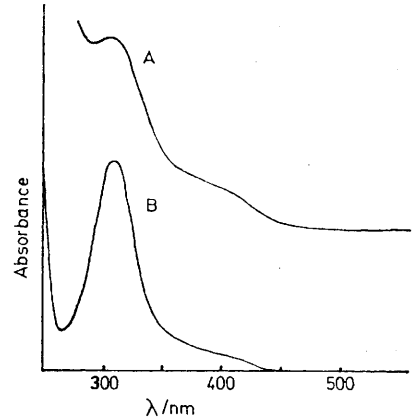

FIGURE 1 Spectrum of $[AuCl_4]^-$. A, Sodium tetrachloroaurate dihydrate crystal; B, 3×10^{-4}M-sodium tetrachloroaurate in 1 M-sodium chloride at pH 4.00

RESULTS AND DISCUSSION

The unpolarised spectrum of a thin film crystal of sodium tetrachloroaurate dihydrate (spectrum A, Figure 1) is very similar to that of the tetrachloroaurate ion in solution (spectrum B, Figure 1; the solution was prepared with an excess of chloride ion to prevent hydrolysis). A Raman study of the same system but with more concentrated solutions gives spectra indicative of a D_{4h} ion and which are almost identical in solid and solution. We therefore consider that the sodium tetra-

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[1] B. I. Peshchevitskii, V. I. Belevatsev, and N. V. Kurbatova, *Zhur. neorg. Khim.*, 1971, **16**, 1898.

[2] D. H. Brown and W. E. Smith, to be published.

[3] R. A. Potts, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1749.

[4] H. Bonomico, G. Dessy, and A. Vaciago, *Atti. Acad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1965, **39**, 504.

chloroaurate crystal is a reasonable model for the tetrachloroaurate ion in solution. Dilution of the solution does not appreciably affect the electronic spectrum of the tetrachloroaurate ion and we conclude, therefore, that it is basically due to a single ion, although we cannot rule out the possibility that some of the obvious intensity differences between solid and solution spectra may be due to interactions.

The $[AuCl_4]^-$ units in the crystal are planar, with a symmetry very close to D_{4h} and they are arranged in parallel planes so that the principal (z) axes are aligned along the b axis of the crystal.[4] If the second-nearest-neighbour environment round the gold atoms is taken into account, the site symmetry of the gold is C_s but we shall show that the spectra arise from a centrosymmetric situation and, consequently, we interpret our results on the basis of a tetragonal field. Since we were able to obtain sufficiently thin crystals in only one orientation, we were precluded from studying the effect of the orthorhombic field produced by the crystal. There was no evidence of orthorhombic or lower symmetry splittings in the quite sharp powder Raman spectrum and no appreciable dichroism in the *ac* plane. This latter piece of evidence is weakened by the fact that there are two different orientations of the $[AuCl_4]^-$ units in the *ac* plane and, consequently, the dichroic effect might be weak. Since the gold atoms do not lie at symmetry points in the *ac* plane, the orthorhombic field would not be centrosymmetric at the gold atoms and thus we believe that, from a crystal as well as an ionic point of view, the tetragonal approximation is reasonable.

We carried out a CNDO calculation, including configuration interaction, using an established program [5] and the results suggest a rather different ordering of the virtual orbitals from that which is conventional (Figure 2). It is the ordering of the excited states which is important from a spectroscopic viewpoint, and the calculation consistently predicts the excited state arising from a $d_{xy} \rightarrow s$ transition to be one of the lowest-energy excited states. Reasonable variations of orbital exponents and geometry do not alter this result appreciably.

The major contribution to all the molecular orbitals involved in the lowest-lying states is from the atomic orbitals of the gold atom, but the ligand contribution can be quite substantial (up to 20—30%). We label the transitions, as others have done, by the gold metal orbital involved but, since these are only symmetry representations for the molecular orbitals, selection rules based on the metal atom quantum numbers will not rigorously apply.

The spectra of $[PtCl_4]^{2-}$ and $[PtBr_4]^{2-}$ have been more extensively studied [6] and we have considered the results obtained from these studies as well as the foregoing calculation in our assignments. There are a number of differences between Au^{3+} and Pt^{2+} which must be taken into account. They are: (i) the existence of lower-lying unfilled s and p orbitals in gold as compared to platinum is indicated both by calculation and by chemistry. Ref. 6 discusses and rejects the assignment of some bands in the Pt^{2+} spectrum to transitions from bonding orbitals to the $d_{x^2-y^2}$ rather than from the d_{xy} and d_{xz},d_{yz} orbitals to higher-energy antibonding orbitals. The rejected assignments for Pt^{2+} are even less likely for Au^{3+}.

(ii) The effect of the higher charge on the ion is to make the d orbitals in Au^{3+} less available for bonding than Pt^{2+} and to increase the metal-ion content of the antibonding orbitals. The calculation suggests that the $d_{x^2-y^2}$ orbital of Au^{3+} is almost a pure gold orbital. The d_{xy} and d_{xz},d_{yz} orbitals do contain appreciable ligand character.

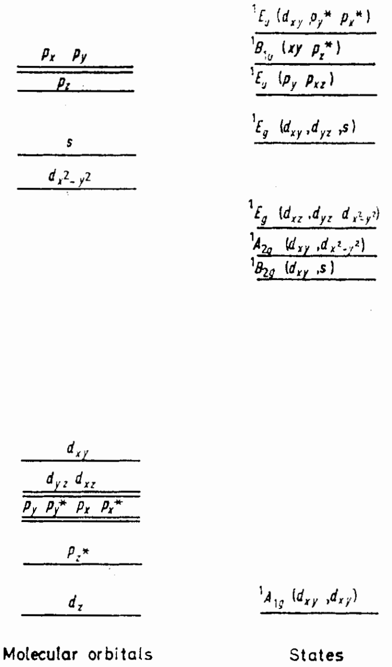

FIGURE 2 Results of a CNDO calculation on $[AuCl_4]^-$. Atomic orbitals specified are the major contributors to the molecular orbitals in each case. Orbitals marked with asterisks are chloride orbitals, all others are gold. The vertical separation indicates the relative energies of the molecular orbitals

(iii) The spectrum of $[PtCl_4]^{2-}$ shows quite well-defined bands due to spin-forbidden transitions at lower energies than those due to spin-allowed transitions. In particular, one of these transitions is to a doubly degenerate excited state and in a magnetic circular dichroism (m.c.d.) study the A term is clearly seen.[7] There are no such spin-forbidden bands in the u.v.–visible spectrum of gold [8] and the m.c.d. spectrum shows no low-energy A term.[7] It seems likely that these spin-forbidden transitions lie close to, or higher in energy than, the corresponding spin-allowed transitions in gold(III).

The selection rules are straightforward. The ground

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[5] D. H. Brown, P. G. Perkins, and J. J. Stewart, *J.C.S. Dalton*, 1972, 1105 and refs. therein.

[6] R. F. Kroening, R. M. Rush, D. S. Martin, and J. C. Clardy, *Inorg. Chem.*, 1974, **13**, 1366, and refs. therein.

[7] A. J. McCaffery, P. N. Schatz, and P. J. Stevens, *J. Amer. Chem. Soc.*, 1968, **90**, 5730.

[8] W. R. Mason and H. B. Gray, *Inorg. Chem.*, 1968, **7**, 55.

state is $^1A_{1g}$. A Laporte-allowed transition to an orbital-singlet excited state will be allowed in *xy* polarisation only, whereas to an orbital doublet it will be allowed in both *xy* and *z* polarisations. The introduction of a vibronic mechanism based on an E_u allowing vibration leads to exactly the same polarisation rules for Laporte-forbidden transitions. Polarised spectra (Figure 3) show two singlet-to-singlet transitions (bands A and B). The assignment of band B to the $^1A_{1g}\rightarrow{}^1E_g(d_{xz},d_{yz}\rightarrow d_{x^2-y^2})$ transition by previous workers[7] is clearly incorrect. The *xy* spectrum cannot be accurately recorded to the peak of band C but this spectrum has been obtained a number of times, using different samples, polars, sources, and sample alignments and we are satisfied that band C has appreciable intensity in the *xy* direction. We consequently assign band C to a singlet-to-doublet transition.

The *z* polarised spectrum shows no bands at lower energy than band C. We have checked this point with solution-grown crystals which are sufficiently thick for band A to have an absorbance >2 and have been able to identify no extra bands. This result is in agreement with comment (iii) that the spin-forbidden transitions evident in $[PtCl_4]^{2-}$ at lower energy than the corresponding spin-allowed ones are at higher energy than the spin-allowed ones in $[AuCl_4]^-$, and suggests that bands A and B are both due to spin-allowed transitions.

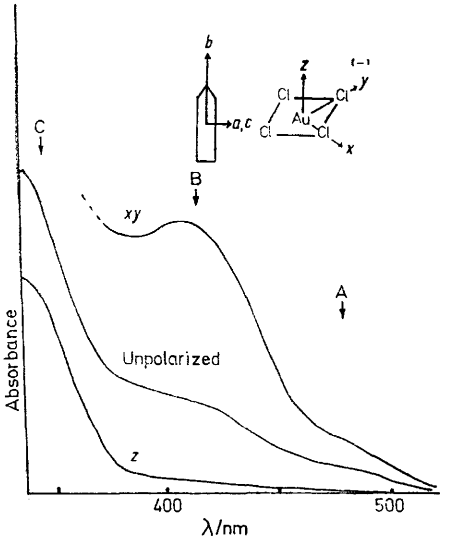

FIGURE 3 Room-temperature polarised spectra of sodium tetrachloroaurate dihydrate

A temperature-dependent study in *xy* polarisation shows that band B is vibronic (Figure 4). The spectra are in agreement with current theories of vibronic intensities showing a shift in peak position to higher energies as the temperature falls and a drop in oscillator strength in agreement with the $f = f_0\coth(h\nu/2kT)$ expression.[9,10] It establishes band B as a Laporte-forbidden electric dipole transition of a centrosymmetric ion and is the main evidence in favour of our tetragonal approximation. Band C is too intense to allow such an accurate assessment of its temperature dependence, but it also appears to be vibronic, and we consider band A to be so also, although in this case the evidence is not conclusive.

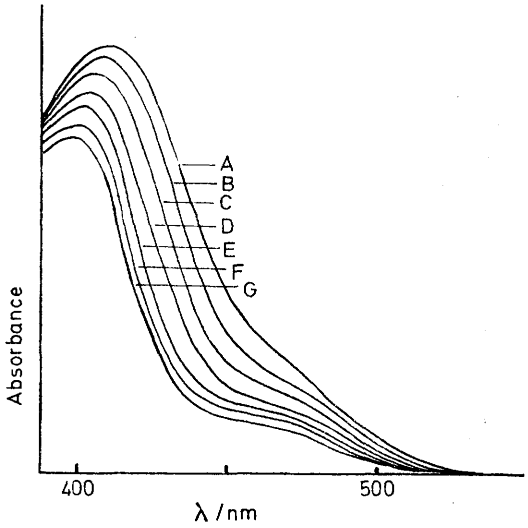

FIGURE 4 Temperature-dependent spectra of sodium tetrachloroaurate dihydrate; temperatures A 294, B 250, C 200, D 150, E 100, F 50, and G 9 K

We assign the bands as follows:

Band A $^1A_{1g}\rightarrow{}^1B_{2g}\ (d_{xy}\rightarrow s)$

Band B $^1A_{1g}\rightarrow{}^1A_{2g}\ (d_{xy}\rightarrow d_{x^2-y^2})$

Band C $^1A_{1g}\rightarrow{}^1E_g\ (d_{xz},d_{yz}\rightarrow d_{x^2-y^2})$

At first sight, the assignment of band A to a strictly forbidden transition is strange, particularly since a possible alternative $(d_{z^2}\rightarrow d_{x^2-y^2})$ is available. Both calculation and intuitive reasoning, however, place the d_{z^2} orbital at a lower energy in the Au^{3+} than in the Pt^{2+} case, and the $d_{z^2}\rightarrow d_{x^2-y^2}$ transition is already considerably higher in energy than the $d_{xz},d_{yz}\rightarrow d_{x^2-y^2}$ transition in $[PtCl_4]^{2-}$. The forbidden nature of the $d_{xy}\rightarrow s$ transition is purely formal, since both metal orbitals mix with different combinations of the same *s* and *p* ligand orbitals and, consequently, the metal-ion quantum numbers are not good quantum numbers for the complex. (In a typical calculation the total orbital contribution of each chloride was 15 and 2% for the d_{xy} and *s* molecular orbitals respectively.) We therefore consider our assignment to be the most reasonable.

These transitions are of very high intensity to be assigned to $d\rightarrow d$ and $d\rightarrow s$ transitions of Au^{3+} but, again, the molecular orbitals described here as d_{xy} and d_{xz},d_{yz} contain a considerable amount of *s* and *p* ligand character, whereas the $d_{x^2-y^2}$ orbital does not. Consequently, any

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[9] A. D. Liehr and C. J. Ballhausen, *Phys. Rev.*, 1957, **106**, 1161.

[10] J. Brynestad, H. L. Yakel, and G. P. Smith, *J. Chem. Phys.*, 1966, **45**, 4652.

distortion, including a vibronic one, away from a centrosymmetric situation will give rise to a transition involving an appreciable ligand L to metal *d* orbital component and, hence, a reasonably intense transition.

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