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Low-Temperature Absorption and Magnetic Circular Dichroism of Gold(III) Tetrachloride Ions in Dicesium Sodium Yttrium Hexachloride

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Received September 10, 1976 AIC60678X

The absorption spectrum at room temperature, liquid nitrogen temperature, and liquid helium temperature and the magnetic circular dichroism at liquid helium temperature have been measured for $AuCl_4^-$:Cs_2NaYCl_6. The results can be explained by assuming the gold ion is present as the tetrachloroaurate ion plus two trans chlorides, i.e., at a site of "six-coordinate" D_{4h} symmetry instead of the O_h symmetry present in the undoped material. No obvious effects of the two trans chlorides were observed. The two observed absorptions are allowed ligand-to-metal charge-transfer transitions. They are assigned, in order of increasing energy, as ${}^1A_{1g} \rightarrow {}^1E_u(\pi) + {}^1A_{2u}$ and ${}^1A_{1g} \rightarrow {}^1E_u(\sigma)$. The transitions to ${}^1E_u(\pi)$ and ${}^1A_{2u}$ overlap but can be distinguished in MCD by their oppositely signed B terms. For ${}^1E_u(\pi)$ $|\mu_z| = 0.2$ (±100%) μ_B. Considerable fine structure was observed at the lowest temperatures in the ${}^1E_u(\pi)$ transition and an assignment is proposed. This structure arises from (1) vibronic transitions involving vibrations of the $AuCl_4^-$ moiety and (2) multiple quanta transitions of lattice vibrations.

Introduction

Square-planar transition metal complexes, via their absorption spectra, have long been a fertile testing ground for molecular orbital theory.[1] Depending on the combinations of metal and ligand any, or all, of the following types of transitions can be observed: d–d, ligand-to-metal charge transfer, metal-to-ligand charge transfer, and intraligand transitions. Most optical studies of these compounds have taken place in solution;[2] however there has recently been some single-crystal work at low temperatures.[3] In addition to allowing the polarization characteristics of the various absorptions to be measured the use of single crystals at low temperatures should provide for improved resolution due to line width narrowing. Unfortunately in most D_{4h} cases this narrowing is insufficient to completely resolve the observed transitions.[4] In only a few cases, all involving d–d transitions, has any vibrational structure been seen. This structure has always been a progression in the totally symmetric (a_{1g}) vibration built on false origins.[3] Thus no information about the excited-state energies of any vibrations except a_{1g} is available.

One example is the absorption and luminescence spectra of $PtCl_4^{2-}$:Cs_2ZrCl_6.[5] The substitution of the divalent platinum ion for the tetravalent zirconium ion is accompanied by the loss of two trans chlorides as charge compensation. This puts the Pt^{2+} ion on a site of D_{4h} symmetry. The net result is that the square-planar $PtCl_4^{2-}$ moiety replaces the octahedral $ZrCl_6^{2-}$ species. The spectra were interpreted primarily using the model of isolated $PtCl_4^{2-}$ molecules and only minimal interaction with the lattice. In that study also only d–d transitions were reported. The major advantage found for this type of substitution was a sharpening of the vibrational structure compared to, for example, pure K_2PtCl_4.

All previous optical studies of gold(III) complexes have been at room temperature.[6] It is well established that the two lowest energy charge-transfer absorptions are ${}^1A_{1g} \rightarrow {}^1A_{2u} + {}^1E_u(\pi)$ and the ${}^1A_{1g} \rightarrow {}^1E_u(\sigma)$, respectively. The ${}^1A_{2u}$ and ${}^1E_u(\pi)$ terms have not previously been resolved for the Au^{3+} ion. Gold(III)–ligand vibrational energies have been well studied. In particular the ground-state vibrational energies in $AuCl_4^-$ of all modes, except the b_{2u} vibration, have been reported.[7] In addition to solution studies the solid-state spectra of $MAuCl_4$ have been studied for various M^+ cations to determine the dependence of the vibrational energies on M^+. For all cases the maximum change observed was ~8%.

The electronic spectra of impurity centers in solids can provide information about the impurity, the host lattice, and the interaction between them. In an attempt to obtain information on each of the above areas and as a part of a continuing study[8] of the elpasolite hexachlorides $Cs_2NaLnCl_6$, Ln = trivalent lanthanide or yttrium(III), the absorption and magnetic circular dichroism (MCD) spectra of $AuCl_4^-$:Cs_2NaYCl_6 have been measured and are reported herein. Previous work involving $Cs_2NaLnCl_6$ has concerned itself with several different types of optical transitions which in turn have monitored different vibrations in the crystal. Ligand-to-metal charge-transfer transitions have been measured for Re^{4+}:Cs_2NaYCl_6[8c] and some gerade vibrations observed. Transitions of this type are also considered in this work.

The d–d transitions in Cr^{3+}:Cs_2NaYCl_6 have been reported.[8e] In addition to several magnetic dipole induced transitions (origins) these Laporte-forbidden transitions gained intensity primarily via vibronic coupling with higher energy ungerade terms. The vibrations observed were assigned as ungerade modes within the model of an octahedral $CrCl_6^{3-}$ moiety interacting only very weakly with the surrounding lattice. In addition to these ungerade modes progressions in a_{1g} and e_g $CrCl_6^{3-}$ moiety vibrations were also observed. This behavior is very different from that observed in the Laporte-forbidden f–f transitions in $Cs_2NaEuCl_6$,[8d] $Cs_2NaPrCl_6$,[9] $Cs_2NaTbCl_6$,[10a] and $Cs_2NaTmCl_6$.[10] In those and other lanthanide cases a density of vibrational states over the entire Brillouin zone was observed. For the most part the vibrations observed corresponded to ungerade modes at the zone center (Γ point). However the contrast between the f–f transitions "sampling" the vibrations of the entire lattice and the d–d transitions seeming to be located totally within the $CrCl_6^{3-}$ moiety is remarkable.

Some of the electric dipole allowed f → d transitions in Ce^{3+}:Cs_2NaYCl_6 have also been reported.[8a] These were the ${}^2F_{5/2}(E''_u) \rightarrow {}^2T_{2g}(U'_g + E''_g)$ transitions. Aside from the no-phonon origins the observed vibronic structure was explained almost entirely in terms of progressions in $S_1(a_{1g})$,[11] the totally symmetric mode of the $Cs_2NaLnCl_6$ "molecule", with low-frequency (~16 and ~46 cm^{-1}) lattice progressions superimposed. Most of the band intensity was found to reside in the latter progressions. Some additional vibrations, which might be one quantum of the Jahn–Teller active modes $S_2(e_g)$ and/or $S_4(t_{2g})$, were also observed. There were, however, no indications of a significant Jahn–Teller effect.

Experimental Section

Absorption and MCD measurements were made at liquid helium temperature at the University of Virginia on a Durrum-Jasco J10B CD spectrophotometer interfaced with a Spex 1400-II $^3/_4$-m double monochromator. Absolute energies from these measurements should be good to ±10 cm^{-1} and energy differences good to ±2 cm^{-1}. Absorption spectra were also recorded at room temperature, liquid nitrogen temperature, and liquid helium temperature on a Cary 14 spectrophotometer. These latter measurements were used to determine relative absorption intensities. The single-crystal sample was mounted in the bore of an Oxford Instruments superconducting magnet system with a field range of 0–55 kG. MCD spectra were recorded at the top field as results indicated no nonlinearities in MCD signal vs. applied field (i.e., no *C* terms were present). In absorption the spectral slit width was 0.15 Å and no features are machine-limited in resolution. Unfortunately the MCD measurements required much greater slit widths and some loss of resolution was noted. This is not too serious as most arguments will be based on the absorption results with the MCD being used mostly as a confirmatory measurement. This does lead, however, to the large errors given below for A/D and B/D. The sample did not polarize the circularly polarized light to any significant extent.

Cs_2NaYCl_6 was prepared by method E of Morss et al.[12] Gold(III) was added as $AuCl_3$, prepared by dissolving the metal in aqua regia and evaporating the resulting solution to dryness. Crystals were grown by the Bridgeman technique as previously described.[8a,b] No chemical analysis was performed on the sample studied and so both absorption and MCD are given in arbitrary units. Note that the parameters of interest, A/D and B/D, are independent of concentration.[13] D is the dipole strength. Transitions due to species other than gold were detected very weakly in absorption and more strongly in MCD. A comparison with a nominally pure sample of Cs_2NaYCl_2 showed these transitions to be present in the undoped crystal as well. These transitions showed a different behavior of their MCD spectrum with temperature variation than those assigned to Au^{3+}; i.e., they showed *C* terms. Thus, they do not arise from transitions on the gold species. Differences of this sort have been noted previously in other systems and have been used to separate overlapping spectra from different species.[14] In no case did these additional transitions overlap those of the gold(III).

Results and Discussion

Before proceeding to a detailed assignment of the observed spectra and vibronic structure a model for the gold(III) site in $CsNaYCl_6$ will be presented. The experimental evidence given below is consistent with the model. Cs_2NaYCl_6 is isomorphous with $Cs_2NaBkCl_6$[12] which has a face-centered cubic structure with four molecules per unit cell. These crystals "have the cubic close-packed arrangement of Cs^+ + $3Cl^-$ layers, with Na^+ and M^{3+} each filling half of the octahedral holes".[15] A good picture of this structure is given in ref 8f. There are three possible substitutional sites for the Au^{3+} ion. One possibility is for it to replace a Cs^+ or a Na^+ ion with the accompanying loss of two unit positive charges from the lattice or two additional Cl^- ions entering the lattice. This would cause a severe disruption and so seems unlikely on these grounds alone. In addition the Cs^+ site is 12-coordinate and this symmetry would not explain the observed spectrum (vide infra), even if the site were distorted. The Na^+ site is six-coordinate, and while a proper distortion of that site would explain the spectrum, the disruption of the lattice just mentioned does mitigate against this being the doped site. This leaves the Y^{3+} site as the only reasonable place for the Au^{3+} to occupy. In the pure crystal this site has six-coordinate, perfect octahedral symmetry and no charge compensation would be required if it were the site of substitution.

The observed spectra, both absorption and MCD, strongly suggest that the species under investigation is either the square-planar $AuCl_4^-$ moiety or, more likely, a strongly tetragonally distorted (D_{4h}) six-coordinate $AuCl_6^{3-}$ with the two trans chlorides at a greater distance from the gold than the four equatorial ones. In essence the $AuCl_4^-$ "molecule" interacts very weakly, if at all, as far as its electronic or vibrational structure is concerned, with two additional trans chlorides. The $AuCl_4^-$ moiety seems to interact somewhat more strongly with the lattice as evidenced in the observed vibrational structure. One way to bring this situation about consistent with the arguments in the preceding paragraph would be for the Au^{3+} to replace a Y^{3+} with a concomitant shortening of four gold–chloride bond lengths. This is reasonable as the gold–chloride bond lengths in $KAuCl_4$[16] are between 2.20 and 2.3 Å while the unperturbed yttrium–chloride bond length in Cs_2NaYCl_6 is about 2.54 Å. This latter distance can be taken as the minimum gold–chloride separation for the two trans chlorides. The d^8 Au^{3+} ion strongly resists any change from a square-planar environment and shortening of the four gold–chloride bonds along with a possible lengthening of the two trans bonds would give rise to D_{4h} symmetry, which, in the strong-field limit suitable to Au^{3+}, would in turn generate a $^1A_{1g}$ (D_{4h} notation) ground state.

With the above model in mind, a word is due here about the treatment of the data, particularly the MCD data. With a tetragonally distorted six-coordinate Au^{3+} site in this cubic crystal there exist three structurally equivalent sites with their fourfold axes arranged in a mutually perpendicular fashion. The crystal used in these studies was not aligned along any particular axis, so an average of the three sites was observed. This situation is equivalent to observing the anisotropic molecules in an isotropic solution and MCD calculations were performed accordingly. The results are the same as previously given for $AuCl_4^-$ in solution,[17] i.e., $A/D = 0$ for the $^1A_{1g} \rightarrow {}^1A_{2u}$ transition and $|A/D| = |\mu/2|$ for the $^1A_{1g} \rightarrow {}^1E_u(\pi)$ transition.

The room-temperature absorption spectrum of $AuCl_4^-$:Cs_2NaYCl_6 shows two broad, featureless bands. One of these is centered at about 30 850 cm^{-1} and the second, roughly 4 times as intense, is centered at about 46 500 cm^{-1}. This agrees well with the ligand-to-metal charge-transfer spectrum of $AuCl_4^-$ in solution. There bands are located at 32 000 cm^{-1} ($\epsilon \sim 5300$) and 44 500 cm^{-1} ($\epsilon \sim 27\,500$).[17] Upon cooling the crystal to ~77 K a general sharpening was observed in both bands along with an increase in optical density and *no* net loss of overall intensity. At this temperature the bands did not shift much in energy and no structure was resolved. At liquid helium temperature (~10 K) the intensity of the two bands remained unchanged but considerable fine structure was resolved on part of the lower energy band. The constant intensity with decreasing temperature strongly indicates the allowed nature of the transitions being observed. No MCD could be recorded for the higher energy transition due to low light levels, and as this band showed no structure in absorption, it will not be considered in any great detail.

The ~10-K absorption and MCD spectra for the band at 3200 Å are shown, under low resolution, in Figure 1. The absorption spectrum shows some asymmetry to the short-wavelength side and the MCD clearly shows the presence of two oppositely signed *B* terms. There is a broad, featureless, negative *B* term which seems to begin at lower energy and has a maximum at about 3190 Å. This is assigned as the $^1A_{1g} \rightarrow {}^1A_{2u}$ transition. There is also a positive *B* term which has a

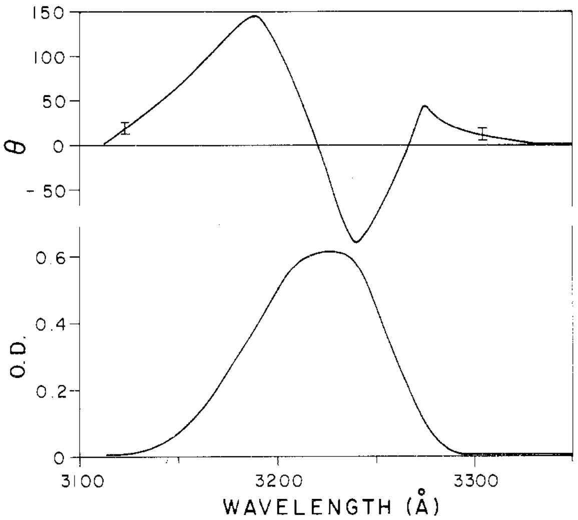

Figure 1. Low-resolution absorption and MCD spectra of the $^1A_{1g} \rightarrow {}^1E_u(\pi) + {}^1A_{2u}$ transitions in $AuCl_4^-$:Cs_2NaYCl_6 at ~10 K. θ is in millidegrees. The MCD spectrum was recorded at $H = 55$ kG. All spectra have been digitized by hand. The noise level is equivalent to the pen width in absorption and is shown as error bars for the MCD.

maximum at about 3260 Å. The lower energy portion of the band shows A terms as well as B terms under higher resolution (Figure 2) and is assigned as the $^1A_{1g} \rightarrow {}^1E_u(\pi)$ transition. An estimate (±100%) of B/D for the two terms can be obtained from their displacements and equations given previously.[18] By using the origin (vide infra) of the $^1E_u(\pi)$ transition it is found that $B/D = +3.0 \times 10^{-3}\ \beta/\text{cm}^{-1}$ for that transition. For the $^1A_{2u}$ transition $B/D = -1.7 \times 10^{-3}\ \beta/\text{cm}^{-1}$. In solution at room temperature $AuCl_4^-$ shows a $B/D = -1.5 \times 10^{-3}\ \beta/\text{cm}^{-1}$ [17] in this energy region. It seems that at higher temperatures the $^1E_u(\pi)$ transition is broadened to such an extent that it cannot be observed.

The calculation of B terms involves sums over all states. In most cases, as in the present one, it is not feasible to calculate with any certainty what either the sign or the magnitude of the B term should be. The present assignment of the $^1E_u(\pi)$ state is unambiguous because of the presence of A terms. With that assignment definite the sign of the B term for that level is observed to be positive. As it is well accepted that the only other term in this energy region is $^1A_{2u}$,[17] the absorption giving rise to the negative B term must be due to that term. The ambiguity in calculated sign extends to the A term for $^1E_u(\pi)$; in the present case the sign of the absolute value of the A term is proportional to the absolute value of the magnetic moment of the excited state.[17]

Figure 2 shows part of the 3200-Å band in both absorption and MCD. Table I lists the energies of the absorption peaks along with their assignments. These will be discussed below in detail. The MCD shows a series of positive A terms and positive B terms. The $^1E_u(\pi)$ state being observed can show no first-order splitting due to spin–orbit coupling as it has zero electron spin. All of the fine structure seen in the spectrum must be due to the interaction of the electronic states with vibrations of the crystalline lattice. While these vibrations represent a density of states over the entire Brillouin zone, a lattice dynamical calculation has not yet been done for Cs_2NaYCl_6 and the vibrations are labeled with their $\vec{k} = 0$ (Γ point) symmetries.

A normal-coordinate analysis has been published for crystals with the elpasolite structure.[11] Ignoring the acoustic modes for the moment, there are five gerade and five ungerade vibrations. It has been shown for $Cs_2NaLnCl_6$[8d,e,9,10] that Laporte-forbidden transitions sample mostly the ungerade modes (so labeled at Γ) and so it is expected that the presently observed Laporte-allowed transitions will interact most strongly with gerade (also at Γ) modes. Additional evidence for this assumption can be seen in the totally different intensity distribution in the vibrations between those presently under study and those in Cr^{3+}:Cs_2NaYCl_6[8c] and the f–f lanthanide transitions.[8d,9,10] For the reduced symmetry in the present case the gerade modes give rise to the following nine vibrations: $S_1(a_{1g})$, $S_2(a_{1g})$, $S_2(b_{1g})$, $S_3(a_{2g})$, $S_3(e_g)$, $S_4(b_{2g})$, $S_4(e_g)$, $S_5(b_{2g})$, and $S_5(e_g)$. Here the S's label the octahedral parent vibrations[11] and the irreducible representations are the symmetries of the actual modes in D_{4h} at Γ.

Vibrations of symmetry e_g cannot show any MCD to first order and need not be considered any further. This leaves six

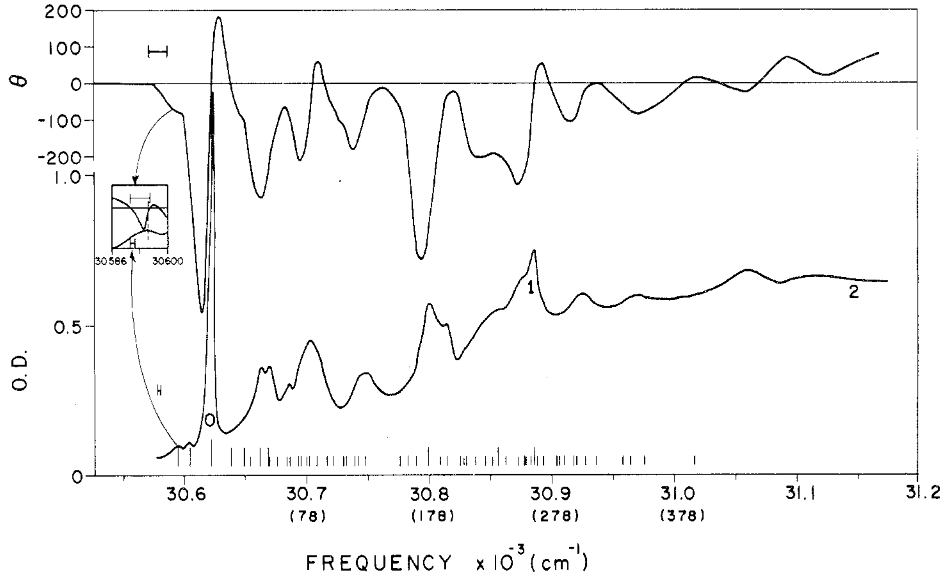

Figure 2. A portion of the 3200-Å transition at ~10 K showing the vibrational structure in the $^1E_u(\pi)$ term. The numbers in parentheses are energies from the origin. Slit widths are indicated for each spectrum. θ is in millidegrees; $H = 55$ kG for the MCD. The positive MCD due to the $^1A_{2u}$ term has been subtracted. The stick spectrum shows the location of absorptions for the proposed vibrational assignments (see Table I and the text). The tallest stick is the electronic origin, next in height are vibronic origins, and the shortest sticks are terms in a progression. No progressions in $S_1(a_{1g})$, except for 0–0, are shown. The noise level is equivalent to the pen width. The insert shows the MCD of the ~27-cm^{-1} hot band under higher resolution.

Table I. Vibrational Structure in the $^1A_{1g} \rightarrow {}^1E_u(\pi)$ Transition in $AuCl_4^-$:Cs_2NaYCl_6

Energy, cm^{-1}		
Obsd[a]	Predicted[b]	Assignment[c-e]
30 595	30 595	ν_2(lattice)–hot band
30 606	30 606	ν_1(lattice)–hot band
30 622	30 622	0–0
30 643(?)[f]	30 638	ν_1 (lattice)
	30 649	ν_2 (lattice)
	30 654	$2\nu_1$
30 662	30 662	ν_3 (lattice)
30 668	30 668	$S_5(b_{2g})$
30 674(?)	30 670	$3\nu_1$
30 681(?)	30 676	$2\nu_2$
30 684	30 684	$S_5 + \nu_1$
	30 686	$4\nu_1$
	30 693	$3\nu_2$
30 694	30 695	$S_5 + \nu_2$
	30 700	$S_5 + 2\nu_1$
30 702	30 702	$2\nu_3$
30 709	30 708	$S_5 + \nu_3$
30 718(?)	30 716	$S_5 + 3\nu_1$
	30 722	$S_5 + 2\nu_2$
	30 730	$4\nu_2$
30 734(?)	30 732	$S_5 + 4\nu_1$
30 740	30 739	$S_5 + 3\nu_2$
30 747	30 742	$3\nu_3$
30 754	30 748	$S_5 + 2\nu_3$
	30 776	$S_5 + 4\nu_2$
30 781	30 782	$4\nu_3$
	30 788	$S_5 + 3\nu_3$
30 798	30 798	$S_4(b_{2g})$
30 813	30 814	$S_4 + \nu_1$
	30 825	$S_4 + \nu_2$
	30 828	$S_5 + 4\nu_3$
	30 830	$S_4 + 2\nu_1$
30 843(?)	30 838	$S_4 + \nu_3$
	30 846	$S_4 + 3\nu_1$
	30 852	$S_4 + 2\nu_2$
30 858	30 858	$S_2(b_{1g})$
	30 862	$S_4 + 4\nu_1$
30 876	30 874	$S_2 + \nu_1$
	30 878	$S_4 + 2\nu_3$
	30 879	$S_4 + 3\nu_2$
30 884[g]	30 884	$S_1(a_{1g})$
	30 885	$S_2 + \nu_2$
	30 890	$S_2 + 2\nu_1$
	30 895	$S_2 + \nu_3$
	30 906	$S_4 + 4\nu_2/S_2 + 3\nu_1$
	30 912	$S_2 + 2\nu_2$
	30 918	$S_4 + 3\nu_3$
	30 922	$S_2 + 4\nu_1$
	30 929	$S_2 + 3\nu_2$
	30 938	$S_2 + 2\nu_3$
	30 958	$S_4 + 4\nu_3$
	30 966	$S_2 + 3\nu_2$
	30 978	$S_2 + 3\nu_3$
	31 018	$S_2 + 4\nu_3$

[a] Measured at ~10 K. [b] Based on energies given in the text and assuming four quanta in each progression. [c] Assignment of the predicted line. This is probably the assignment of the observed line shown. See Figure 2 to compare predicted and observed spectra. [d] The notation is defined in the text. [e] Every line is repeated + $S_1(a_{1g})$ but only the repeat of the 0–0 line is shown explicitly. [f] (?) indicates a probable shoulder in the absorption spectrum. [g] At energies greater than 30 884 cm^{-1} the spectrum broadens considerably. Transitions in this region will include those predicted plus repeats of lower energy lines in $S_1(a_{1g})$.

vibrations which can be observed. Two of these modes, $S_3(a_{2g})$ and $S_5(b_{2g})$, are essentially "lattice" modes and will have very low energy. The former is a "librational" mode which is usually not observed, while the latter will involve motion of the Cs^+ ions only.[11] Three of the remaining vibrations $S_1(a_{1g})$, $S_2(b_{1g})$, and $S_4(b_{2g})$ can be directly correlated with modes of the same symmetry in $CsAuCl_4$[7] and can be considered "moiety" modes. They are respectively the symmetric in-plane stretch ν_1, the antisymmetric in-plane stretch ν_3, and the in-plane bending mode ν_4. These vibrations will appear at higher energy than the "lattice" modes and their energies will be compared with those in $CsAuCl_4$.[7] The remaining vibration, $S_2(a_{1g})$, will involve the symmetric stretching of the two trans chlorides. If observed, this vibration will also be at low energy.

The most striking feature in the liquid helium temperature spectrum is the extremely sharp (~5 cm^{-1} half-width) intense absorption at 30622 cm^{-1}. This feature broadens very rapidly as the temperature is raised, as do all of the fine structure lines. This line is assigned as the nonphonon (0–0) transition $^1A_{1g} \rightarrow {}^1E_u(\pi)$ and is labeled 0 in Figure 2. The MCD associated with this transition shows a positive A term and a positive B term. An estimate of A/D (=+ 0.1 μ_B) for this origin was obtained in the same manner for B/D.[18] This leads to a value of $|0.2|$ for the magnetic moment of the $^1E_u(\pi)$ state. This is the same order of magnitude as the magnetic moment measured in solution for the $^1A_{1g} \rightarrow {}^1E_u(\sigma)$ transition (i.e., there $|\mu| = 0.32\ \beta$) and is additional evidence for the charge-transfer nature of the excited state.

An unambiguous assignment of all of the vibrational structure is not possible without a detailed lattice dynamical calculation, the problem being particularly acute in the low-energy region. There is also the added difficulty in the present case that all vibrations may not be resolved. In addition to those peaks and shoulders that are resolved in the absorption spectrum, some of which are not visible on the scale of Figure 2, there are indications of many other, weaker, shoulders as well as the possibility of unresolved bands present under the broader absorptions. The assignments given (Table I) below, while not unique, are consistent with the observed spectrum and reasonable when comparisons are made to the isolated $AuCl_4^-$ species[7] and to Re^{4+}:Cs_2NaYCl_6[8c] and Ce^{3+}:Cs_2NaYCl_6,[8a] the other cases of a Laporte-allowed transitions in this host. In addition to the observed spectra Figure 2 shows a stick spectrum of the expected positions of lines based on the proposed vibrational energies.

Keeping in mind the comments made above about individual vibrations, the observed spectrum can be assigned in the following way. The two very weak lines to the lower energy side of 0 are hot lattice (possibly acoustic) modes. The energy of one of them, 16 cm^{-1}, corresponds to an observed hot band in Ce^{3+}:Cs_2NaYCl_6.[8a] Upon increasing the resolution in MCD the 27-cm^{-1} line showed a positive A term and a positive B term (Figure 2 inset) indicating its origin to be absorption by the $^1E_u(\pi)$ term. Even under these higher resolution conditions the 16-cm^{-1} line could not be resolved in MCD. Just as in Ce^{3+}:Cs_2NaYCl_6,[8a] neither of these transitions is resolved on the high-energy side of the origin, although a weak shoulder is indicated at ~21 cm^{-1}. Additional quanta of these modes and progressions in these modes built on other origins are possibly present.

The next obvious feature is an absorption at 40 cm^{-1} from 0. (Note that all energies given below are measured from the 0 line unless otherwise stated.) This is the first term in a progression which gives rise to bands at 2, 3, and 4 times 40 cm^{-1}. This vibration probably corresponds to the ~46-cm^{-1} (acoustic) mode observed in Re^{4+}:$CsNaYCl_6$[8c] and Ce^{3+}:Cs_2NaYCl_6.[8a] The next line observed at 46 cm^{-1} is assigned as $S_5(b_{2g})$. *No progression with a spacing of 46 cm^{-1} is present.* This line serves as an origin for a progression of three or four terms with a 40-cm^{-1} separation between the components. The 46-cm^{-1} line also serves as an origin for progression in the 16- and 27-cm^{-1} modes, three or four quanta of which are present for each vibration.

The absorption at 176 cm^{-1} is assigned to $S_4(b_{2g})$. This vibration is about the same energy as the equivalent vibration in $CsAuCl_4$[7] and close to the same energy as the O_h parent vibration $S_4(t_{2g})$, in Re^{4+}:$CsNaYCl_6$.[8c] This line also serves as an origin for progressions in the 16-, 27-, and 40-cm^{-1} vibrations. The next vibration in order of increasing energy is the $S_2(b_{1g})$. It is expected that this mode will show about the same percent reduction in energy as the $S_1(a_{1g})$ mode upon going from the ground state to the $^1E_u(\pi)$ state (vide infra). This would place $S_2(b_{1g})$ at $\sim$242 cm^{-1}. The closest resolved absorptions are at 236 and 254 cm^{-1}. The 254-cm^{-1} absorption can be accounted for on the basis of combination bands (see Figure 2 and Table I) but the 236-cm^{-1} absorption cannot be so explained and is assigned as $S_2(b_{1g})$. This transition also serves as an origin for progressions in the 16-, 27-, and 40-cm^{-1} vibrations.

The next band to be identified is at 262 cm^{-1}, labeled 1 in Figure 2, and is assigned as $S_1(a_{1g})$. The next line in this progression would be at 2. The parent O_h vibration $S_1(a_{1g})$ is at $\sim$300 cm^{-1} in Ce^{3+}:Cs_2NaYCl_6[8a] and at $\sim$305 cm^{-1} in Re^{4+}:Cs_2NaYCl_6.[8c]

The 262-cm^{-1} band is a 25% reduction from the ground-state energy of $\nu_1(a_{1g})$ in $CsAuCl_4$.[7] This large reduction in energy is the result of exciting an electron from a bonding orbital ($e_u(\pi)$), along which there is a component of the vibration, into an antibonding orbital ($b_{2g}{}^*(x^2 - y^2)$) which is along the direction of motion of the vibration. These same conditions hold for the $S_2(b_{1g})$ vibration and it shows about a 28% reduction. For the $S_5(b_{2g})$ vibration there is no component along the $b_{2g}{}^*$ orbital and so the only reduction in energy will result from the component of this vibration along the $e_u(\pi)$ orbital.

The one vibration that has not yet been identified is $S_2(a_{1g})$. Due to the larger gold–chloride separation for the trans chlorides, as compared with the four in-plane chlorides, this mode will have an energy less than half that of $S_1(a_{1g})$ in the ground state. This energy should not change very much in the $^1E_u(\pi)$ state. Two possibilities for this mode are absorptions at 62 or 125 cm^{-1}. Each of these could be the first term in a progression of the given energy or components of other progressions. Neither of these two lines shows progressions in the 16-, 27-, and 40-cm^{-1} modes. At this point there is no way to determine which of these energies corresponds to $S_2(a_{1g})$ or, for that matter, if this mode is observed at all. Experiments are planned with $AuBr_4^-$:Cs_2NaYCl_6 which may clarify this situation.

Thus far the effects of the two trans chlorides on the electronic spectrum have not been considered. These ligands will introduce four additional filled molecular orbitals: $a_{1g}(\sigma)$, $a_{2u}(\sigma)$, $e_u(\pi)$, and $e_u(\pi)$. The only allowed transition to $b_{2g}{}^*$ will be from $e_u(\pi)$, the result being another $^1E_u(\pi)$ state. Elementary molecular orbital theory places the transition to this state at lower energy than the $^1E_u(\pi)$ state from the four in-plane chlorides (i.e., the $e_u(\pi)$ orbital from the trans chlorides will be higher in energy than the $e_u(\pi)$ orbital from the in-plane chlorides), at about the same energy expected for the d–d transitions. The absorption spectrum of $AuCl_4^-$:Cs_2NaYCl_6 has been measured down to 20000 cm^{-1} and no absorption was observed. Thus, the interaction of the gold and the two trans chlorides is seen to be very weak and to not noticeably change the electronic spectrum from that observed with $AuCl_4^-$.

Acknowledgment. The author thanks Dr. Paul N. Schatz for the use of his equipment. Various aspects of this work were discussed with Dr. B. J. Hales, Dr. K. N. Houk, Dr. S. P. McGlynn, Dr. S. B. Peipho, and Dr. W. C. Yeakel. This work was supported, in part, by a Summer Faculty Fellowship from the LSU Council-on-Research.

Registry No. $AuCl_4^-$, 14337-12-3; Cs_2NaYCl_6, 27880-16-6.

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(19) The author thanks Dr. J. C. Collingwood for first bringing these expressions to his attention.