Charge Transfer Spectra of some Gold(III) Complexes

Arun Kumar Gangopadhayay and Animesh Chakravorty

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crease the $-(F^0-H_0^0)/RT$ values given here by 0.061 as compared to the data of reference 6. The data for CO_2 are in good agreement with previously published data.

It has just come to the authors' attention that thermodynamic functions for CO_2, COS, CS_2, NO_2, and SO_2 have recently been published in the *Journal of Chemical and Engineering Data* **6**, 390 (1961). Agree-

ment is fair to good. Differences are probably due to somewhat different methods of calculation and to some differences in spectroscopic constants.

Charge Transfer Spectra of some Gold(III) Complexes

Arun Kumar Gangopadhayay and Animesh Chakravorty

Department of Physical Chemistry, University College of Science, Calcutta-9, India

(Received May 22, 1961)

Tetrahalo complexes of Au(III) show two intense bands in the ultraviolet. These are interpreted as charge-transfer bands; the transfer is from halogen p to gold d orbitals. The two bands are associated with $p_\sigma \rightarrow d_{x^2-y^2}$ and $p_\pi \rightarrow d_{x^2-y^2}$ transitions. The iodo complex undergoes spontaneous reduction; reason for this is discussed. The ethylenediamine complexes of Au(III) also exhibit interesting charge-transfer phenomenon.

IN the third transitional series two familiar ions with eight electrons in the outermost d shell are Pt^{2+} and Au^{3+}. They generally form four coordinate square-planar complexes which are almost invariably spin paired and hence diamagnetic. Spin pairing is facilitated by the large extension of the $5d$ electron clouds into space. In valence-bond language, Pt (II) and Au (III) complexes involve dsp^2 hybridization; in crystal-field nomenclature they almost always belong to "strong field" class. The planarity of some such complexes has been proved by x-ray crystallography[1,2] or otherwise.[3]

The visible and uv spectra of platinous complexes of the type $[Pt(NH_3)_nCl_{4-n}]^{(n-2)+}$, where $n=0-4$, have been interpreted by Chatt *et al.*[4] in terms of the crystal-field theory. The transitions involved are all within the $5d^8$ system of Pt(II): $d_{xy} \rightarrow d_{x^2-y^2}$; $d_{xz}(d_{yz}) \rightarrow d_{x^2-y^2}$; $d_{z^2} \rightarrow d_{x^2-y^2}$. They are of forbidden g-g type and accordingly have low molar extinction coefficients, generally less than 100. The triplets, which attain considerable intensity in the $5d$ series due to strong spin-orbit interaction, have much smaller extinction values.

The isoelectronic Au(III) complexes should show similar bands which, however, will be shifted to shorter wavelengths compared to those of Pt(II) complexes because of the higher charge and smaller size of Au(III). But just these factors increase its electronegativity and

electron affinity over those of Pt(II). One chemical manifestation is the higher oxidizing power of Au(III). Spectrochemically we may expect that in combination with ligands of relatively low ionization potential, Au(III) complexes will show electron-transfer bands in the uv or visible region. The spectra of tetrahalo complexes of Au(III) were accordingly studied. Au(III) ethylenediamine complexes have an interesting bearing in this problem.

EXPERIMENTAL

$KAuBr_4 \cdot 2H_2O$ was prepared and purified following a standard method.[5] The tetrachloro complex could be obtained by decomposing the bromo complex with aqua regia. Excess nitric acid was removed by repeated evaporation with concentrated HCl. The final product could be obtained anhydrous by crystallization from alcohol.[2] The ethylenediamine monohydrate was E. Merck reagent, and it was distilled twice before use so as to get a perfectly colorless and transparent product. The potassium chloride, bromide, and iodide were all E. Merck G.R. quality. The water used was double-distilled.

Spectral measurements were carried out in 1-cm matched silica cells in Beckman spectrophotometer, model DU. Balancing was done against proper solutions e.g., for $KAuBr_4 \cdot 2H_2O$ in $1N$ KBr; $1N$ KBr was used as the standard. In the study of Au(III) ethylenediamine complexes a relatively concentrated solution of $KAuCl_4$ or $KAuBr_4 \cdot 2H_2O$ was made in 10% ethylene-

[1] R. G. Dickinson, J. Am. Chem. Soc. **44**, 2404 (1922).
[2] E. G. Cox and K. C. Webster, J. Chem. Soc. **1936**, 1635.
[3] A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, New York, 1950), p. 625.
[4] J. Chatt, G. A. Gamlen, and L. E. Orgel, J. Chem. Soc. **1958**, 486.
[5] *Inorganic Syntheses*, edited by J. C. Bailey, Jr., (McGraw-Hill Book Company, Inc., 1953), Vol. IV, p. 14.

diamine hydrate. An aliquot from this was diluted with the same 10% ethylenediamine such that optical densities had reasonable values. Another equal aliquot was diluted with $2N$ HClO$_4$ (the whole of ethylenediamine is neutralized) to the same volume. Thus the concentration of Au(III) was same in the two solutions.

Solutions of KAuBr$_4$·2H$_2$O and KAuCl$_4$ were made by direct weighing. Since we are not quite sure about the hydration of KAuCl$_4$ (the anhydrous salt might absorb some water during weighing), we do not claim any great accuracy in the extinction values. Measurements had to be carried with different concentrations, since the peaks have very different intensities. Concentrations were so chosen that O.D. was generally between 0.2 to 0.5 near the band maxima.

RESULTS AND DISCUSSION

Spectra of KAuCl$_4$ and KAuBr$_4$ were measured in $1N$ KCl and $1N$ KBr, respectively. This was mainly to avoid to possible aquation or hydrolysis. The spectrum of KAuCl$_4$ $1N$ KCl is very similar to that in $1N$ HCl, which has already been reported by one of us.[6] Under such high concentrations of halide ions it is quite possible that higher complexes, e.g., [AuX$_5$]$^{2-}$ or [AuX$_6$]$^{3-}$, are formed to some extent with one or two "long" Au-X bonds. This point is discussed later.

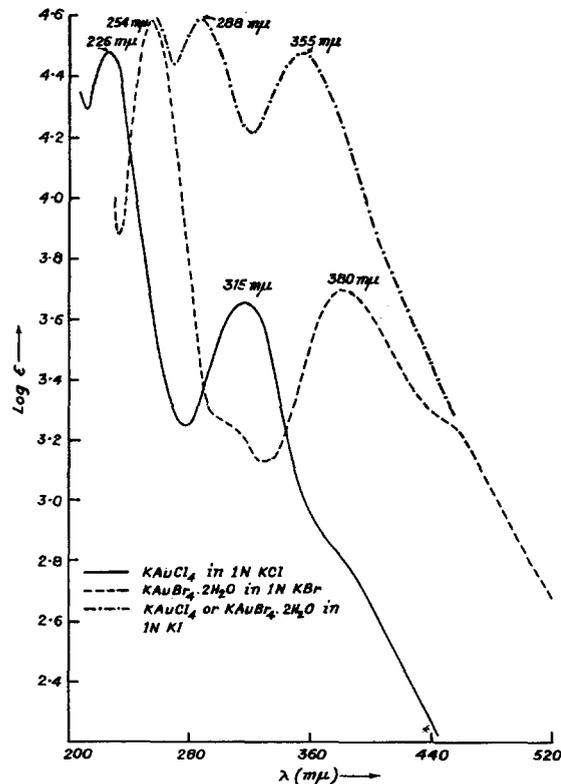Both [AuCl$_4$]$^-$ and [AuBr$_4$]$^-$ show two strong bands

FIG. 1. Spectra of KAuX$_4$ in $1N$ KX.

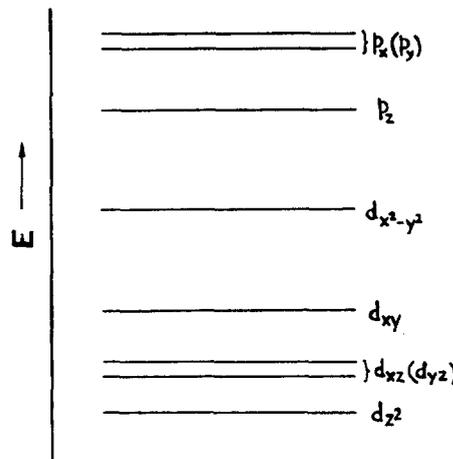[6] A. Chakravorty, Naturwissenschaften (to be published).

FIG. 2. Splitting of $5d$ and $6p$ orbitals in tetragonal ligand-field (not drawn to scale).

in the uv (Fig. 1). The band at lower wavelength (henceforth called λ_1) is about seven times more intense than the other (λ_2). The bands of the bromo complex are placed at longer wavelengths than those of the chloro complex. The high extinction coefficients clearly indicate that these are not crystal-field transitions within the metal d shell, but must correspond to some $g \rightarrow u$ or $u \rightarrow g$ type allowed transition.

λ_1 cannot possibly be due to $5d \rightarrow 6p$ transition in the gold atom since this would mean too small an energy gap between the two levels. Further, there is no reason why such a band should show a large forward shift in passing from the chloro to the bromo complex. Let us consider a simple electrostatic picture for [AuX$_4$]$^-$. The Au^{3+} ion is at the origin and the four X$^-$ are placed on the x and y axes. The d orbitals will then be split up in the following order[4] of decreasing energy: $d_{x^2-y^2}$, d_{xy}, $d_{xz}(d_{yz})$, d_{z^2}. In the $6p$ shell, p_x and p_y will be destabilized since they point directly towards the ligands, p_z remaining unaffected hence most stable. This is shown in Fig. 2.

On passing from [AuCl$_4$]$^-$ to [AuBr$_4$]$^-$, the position of p_z is unaffected; the p_x, p_y, and the d orbitals are somewhat stabilized since Cl$^-$ exerts greater repulsive force than Br$^-$, due mainly to smaller size and closer approach. The longest wavelength $d \rightarrow p$ transition will then involve the p_z orbital in the excited state and hence should shift to shorter wavelength on passing from [AuCl$_4$]$^-$ to [AuBr$_4$]$^-$ while reverse is the case. Further, ethylenediamine is known to produce much stronger perturbation than the Cl$^-$, so that for [Auen$_2$]$^{3+}$ the longest wavelength $d \rightarrow p$ band should be at a wavelength higher than that for [AuCl$_4$]$^-$. In fact, however, λ_1 for [Auen$_2$]$^{3+}$ is not reached even at 200 mμ. The above arguments are based on a crude model, but the results should be qualitatively true, so that λ_1 can hardly be a $d \rightarrow p$ transition.

We believe that λ_1 and λ_2 represent electron transfer from ligand orbitals to holes in the $5d$ shell of Au(III).
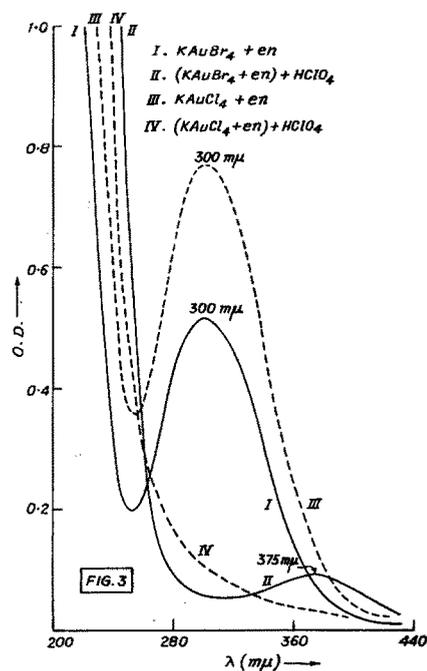
FIG. 3. Spectra of (KAuX₄+en) and (KAuX₄+en)+HClO₄ systems (en=ethylenediamine).

The shift to longer wavelengths in bromo over chloro complex is then understandable on the basis of lower ionization potential of Br⁻. This shift is quite general in halides.[7] The two bands cannot be correlated to $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states of the halogen atom produced in the excited state of the complex, since the observed energy gaps between λ_1 and λ_2 are much too large. The difference of above two states is: Cl=880 cm⁻¹, Br=3700 cm⁻¹, while $\Delta\lambda$ for [AuCl₄]⁻ is 12 500 cm⁻¹ and for [AuBr₄]⁻ is 13 050 cm⁻¹.

At this point it is relevant to consider a qualitative molecular orbital picture for square planar complexes.[8] With same placement of ligands as required in Fig. 2, the $5d_{x^2-y^2}$, $6s$, $6p_x$, and $6p_y$ orbitals of Au(III) will "overlap" σ orbitals of the ligands, viz., ns, np_x, np_y ($n=3$ for Cl⁻ and 4 for Br⁻) giving rise to four bonding and four antibonding orbitals. The former will be occupied by eight "coordinated" electrons from the ligands, the latter remaining empty. The metal orbitals d_{xy}, $d_{xz}(d_{yz})$, and d_{z^2} are nonbonding receiving eight metal electrons, all paired. The sixteen π electrons (the "lone pairs") on the four halide ions may somewhat destabilize the filled d_{xy} set through π interaction but the halogen p_z and empty metal-$6p_z$ orbitals will be mutually stabilized through π bonding. The π electrons are necessarily less stable than σ electrons.
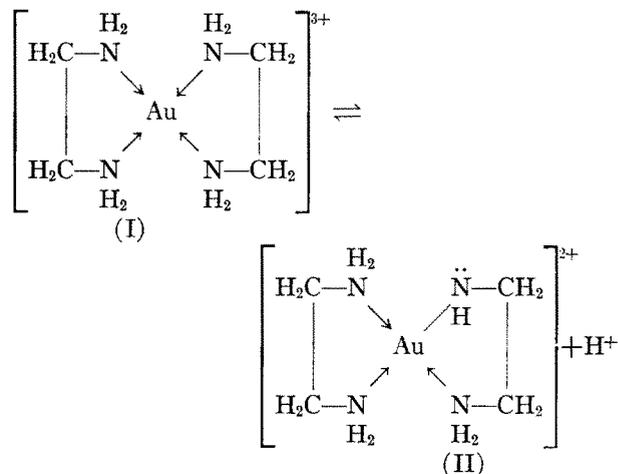
The following assignments are now made. λ_1: transition from highest filled bonding orbital to lowest unfilled antibonding orbital, i.e., roughly a $p_\pi \rightarrow d_{x^2-y^2}$ transition, while λ_2 is $p_\pi \rightarrow d_{x^2-y^2}$. The former is a $g \rightarrow u$ type transition, and since the σ overlap is also quite considerable, the intensity will be very high, as is

actually the case. $p_\pi \rightarrow d_{x^2-y^2}$ is also $g \rightarrow u$ type, but since there is very little overlap, intensity should be quite low. It is to be noted that $d_{x^2-y^2}$ is not pure gold orbital, but is mixed with halogen σ orbital, which in turn is a hybrid of p and s, so that the transition $p_\pi \rightarrow d_{x^2-y^2}$ will have some character of the strongly allowed $p_\pi \rightarrow s$ transition in the halogen. The considerable π mixing of halogen p_π and metal $6p$ orbitals especially of p_z with an empty $6p_z$ gold orbital, will also add to the intensity of the $p_\pi \rightarrow d_{x^2-y^2}$ transition. The relatively high intensity of $p_\pi \rightarrow d_{z^2}$ transition in [Co(NH₃)₅X]²⁺ has been similarly interpreted by Yatemera.[9] In any case, the intensity of λ_2 will be much smaller than λ_1, as is actually the case. Harris and Reece[10] have shown that in a *nonaqueous* medium like nitrobenzene or nitromethane, [AuBr₄]⁻ reacts with Br⁻ to give [AuBr₆]³⁻. During this process λ_2 shows a blue shift and its intensity undergoes a ninefold decrease (from $\epsilon=4850$ to $\epsilon=550$). Formation of [AuBr₆]³⁻ can be explained on the basis of two "long" $6p_z6d_{z^2}$ bonds along the z axis, i.e., normal to the original planar molecule. Thus the $6p_z$ metal orbital is filled up and can no longer form π bond with halogen p_z. The decrease in intensity of λ_2 is possibly associated with this factor. The high intensity of λ_2 in $1N$ *aqueous* KBr tends to indicate that higher complexes like [AuBr₆]³⁻ are not formed in appreciable concentration.

Strong support in favor of the above assignment of λ_2 is further obtained from studies on spectra of bis-ethylenediamine-Au(III) complexes.[11] [Au(en)₂]³⁺ (en=ethylenediamine) acts as a monoacid base of $P_K=6.5$, ionizing as follows:

$$
\begin{bmatrix}
\overset{H_2}{H_2C-N} \quad \overset{H_2}{N-CH_2} \\
\diagdown \quad \diagup \\
Au \\
\diagup \quad \diagdown \\
H_2C-N \quad N-CH_2 \\
H_2 \qquad H_2
\end{bmatrix}^{3+}
\rightleftharpoons
$$

(I)

$$
\begin{bmatrix}
\overset{H_2}{H_2C-N} \quad \overset{..}{N}-CH_2 \\
\diagdown \quad \diagup H \\
Au \\
\diagup \quad \diagdown \\
H_2C-N \quad N-CH_2 \\
H_2 \qquad H_2
\end{bmatrix}^{2+}
+H^+
$$

(II)

In an alkaline medium the ion II is mainly present; on acidification it is neutralized to I. Since ethylenediamine itself is basic, when an excess of this material is added to KAuBr₄ or KAuCl₄, the halogen atoms are replaced and ion II is produced. Both I and II were isolated[11] in the crystalline state as chloride or bromide.

In II, there is a pair of π electrons on one of te hnitro-

[7] L. E. Orgel, Quart. Revs. (London) **8**, 452 (1954).
[8] J. H. Van Vleck, J. Chem. Phys. **3**, 803 (1935).
[9] H. Yatemera, J. Inorg. & Nuclear Chem. **15**, 50 (1960).
[10] C. M. Harris and I. H. Reece, Nature **182**, 1665 (1958).
[11] B. P. Block and J. C. Bailer, Jr., J. Am. Chem. Soc. **77**, 6152 (1955).

gen atoms so that a band representing $p_\pi \rightarrow d_{x^2-y^2}$ transition should be present. In $[Auen_2]^{3+}$, however, such a band is not expected for obvious reasons.

A solution of $KAuCl_4$ in 10% ethylenediamine hydrate gives a peak at 300 mμ with $\epsilon = 2600$ (Fig. 3). In the solution acidified with $2N$ $HClO_4$, the band is completely quenched. Thus our expectations are fulfilled. If $KAuBr_4$ is replaced for $KAuCl_4$ identical results (Fig. 3) are obtained except for the fact that in acidic medium there is a relatively weak and broad band at 375 mμ ($\epsilon = 460$). It cannot be a crystal-field band, for then it should be present in $[Auen_2]Cl_3$ as well. This band may be due to charge transfer between $[Auen_2]^{3+}$ as a whole and bromide ions. Linhard[12] has observed similar interionic charge transfer in the $[Co(NH_3)_6]^{3+}$ $+I^-$ system. The work has been extended by Japanese workers[13] to copper(II) complexes, e.g., $[Cuen_2]^{2+}$. It is relevant to note that Block and Bailer[11] reported $[Auen_2]Cl_3$ as colorless and $[Auen_2]Br_3$ as light yellow in the crystalline state. The most probable interpretation of this unexpected color variation is the one suggested above. An analogous case is known in the amine complexes of trivalent Ir; viz., $[Ir(NH_3)_6]X_3$, when $x = Cl$ or Br, the complex is colorless; when $x = I$, yellow. A similar interpretation has been suggested.[7]

In 10% ethylenediamine it was not possible to follow the spectra beyond about 230 mμ due possibly to the strong absorption of OH^- ions which made the blank opaque. So λ_1 could not be located for II. In the acidic solutions where I was present, this limitation disappeared. The absorption increases steeply but the peak is not reached even at 200 mμ. This is quite expected since the ionization potential of the lone pair (this pair is involved in the σ bond of complex) in

$$:N\overset{\diagup}{\underset{\diagdown}{\rule{1.5em}{0.4pt}}}$$

is much larger than that of chloride ion; in $[AuCl_4]^-$ the band is at 226 mμ. This expected shift of charge-transfer bands to shorter wavelengths as we pass from bromo to chloro to amine complex is quite general, e.g., in Co(III) complexes.[14]

Case of the Iodo-Complex

When $KAuCl_4$ is dissolved in $1N$ KBr the reaction $KAuCl_4 + 4KBr = KAuBr_4 + 4KCl$ occurs rapidly and the solution gives a spectrum which is that of $KAuBr_4$. A solution of $KAuCl_4$ or $KAuBr_4$ in $1N$ KI may similarly be expected to produce $KAuI_4$. But such solutions gave spectra characteristic of the I_3^- ion—two roughly equally strong bands (ϵ calculated on the basis of gold-concentration) (288 mμ, $\epsilon = 39\ 000$; 355 mμ, $\epsilon = 30\ 000$) with energy gap 6670 cm^{-1} (Fig. 1). The solutions produced intense coloration with starch. Thus $[AuCl_4]^-$ and $[AuBr_4]^-$ are reduced by KI under the present

experimental conditions. It is to be noted that $[AuI_4]^-$ is not unknown, the potassium salt has been described as a black solid[15] which is thermally quite unstable, liberating iodine.

We believe that in the present experiments, iodo complexes are formed first only to decompose rapidly. This behavior can be explained as follows. In going from chloro to bromo complex the charge-transfer bands are shifted to longer wavelengths and this should continue in the iodo complex. In fact, the shift between bromo-iodo pair is expected to be much larger than that in the chloro-bromo pair due to larger change in ionization potential in the former pair. By simple arguments[7] it can be shown that when a charge-transfer band moves into the near infrared, spontaneous oxidation-reduction becomes possible kinetically as soon as the tail of the band approaches zero frequency. This we believe is the case with the iodo complex in the present conditions. A kinetics study could give useful information. The kinetics of reaction between Fe^{3+} and I^- has been interpreted[16] via the intermediary formation of iodo complex.

It may be noted that the situation with simple Au(III) halides AuX_3 which in fact are halogen bridged complexes[3] through demerization, is quite similar. $AuCl_3$ (red), $AuBr_3$ (dark brown) are stable; AuI_3 (green) decomposes soon into AuI and I_2 at 25°C.

CONCLUDING REMARKS

The evidences given are not enough to make the assignments of λ_1 and λ_2 unequivocal. Studies on polarization selectivity of the two bands in single-crystal spectra might give very useful information about their origin, e.g., $p_\sigma \rightarrow d_{x^2-y^2}$ band is expected to be polarized in the xy plane since the excited state has the symmetry E_u, which also is the symmetry of x and y axes in D_{4h} group. The crystal spectrum of $CsAuCl_4$ has been reported by Japanese workers.[17] Unfortunately the crystal structure is not known and further the crystal spectrum is so much different from solution spectrum that no definite correlation seems possible.

It is fortunate that $KAuX_4$ is soluble in a variety of nonaqueous solvents. Shifts in λ_1 and λ_2 with change in solvent polarity could give interesting information. In fact, λ_1 and λ_2 show red shifts with decreasing polarity of the solvent. This point is now being closely investigated.

The shoulders on the tail of λ_2 in the spectra of $[AuCl_4]^-$, $[AuBr_4]^-$ (Fig. 1) possibly represent crystal field transitions some of which might have been completely obscured by the intense charge transfer bands.

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[14] M. Linhard and M. Weigel, Z. anorg. u. allgem. Chem. **266**, 49 (1951).
[15] N. V. Sidgwick, *The Chemical Elements and their Compounds* (Oxford University Press, New York, 1950), p. 190.
[16] A. J. Fudge and K. W. Sykes, J. Chem. Soc. **1952**, 119.
[17] S. Yamada and R. Tsuchida, Bull. Chem. Soc. Japan **29**, 424 (1956).