teractions will be with ligands bonded at 90° to the $\pi$-electron-withdrawing group. There are two such 90° neighbors in the trigonal bypyramid transition state for the replacement of the *trans* ligand, but three such neighbors in the replacement of a *cis* ligand in the transition state. Therefore, the electron withdrawal may deactivate the transition state in *cis* substitution. Thus the ethylene in the $[Pt(C_2H_4)Cl_3]^-$ ion of Zeise's salt virtually labilizes the *trans*-chloride but reduces the rate of acid hydrolysis of the *cis*-chloride by a factor of 0.15.[15] A negative ion, such as chloride, is therefore especially effective in *cis* deactivation in comparison to its rather weak *trans* activation. Hence the ligand repulsions which are important in the equilibrium *trans* effect can be considered to exert a strong influence on the kinetics also.

Finally, it seems appropriate to comment that the great utility of the *trans* effect has focused attention upon differences in rates which are frequently rather modest. It is certainly an ambitious and formidable requirement for the models of bonding in the coordination complexes, which are admittedly crude, that they predict differences of the order of 0.4 kcal./mole in activation energies of the respective reactions.

[15] S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

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# The Luminescence of Thallium(I) Halo Complexes

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Excitation and emission spectra of solutions of KCl, KBr, and KI containing thallium(I) have been obtained by means of a spectrophotofluorometer. The emission spectra of the chloride and bromide solutions were analyzed using previously determined dissociation constants for the halo complexes of thallium. For coordination number $n$ = 0, 1, 2, 4, emission peaks lie at 370, 435, 435, and 450 m$\mu$, respectively, for $TlCl_n^{1-n}$ and at 370, 440, 475, and 495 m$\mu$, respectively, for $TlBr_n^{1-n}$.

## Introduction

When a small amount of a thallium(I) halide is added to a solution of an alkali halide, new absorption and emission bands, which are not characteristic of the alkali halide itself, are observed. Investigations of the ultraviolet absorption spectra of alkali halide solutions containing thallium(I) halide by Fromherz and Lih,[1] and of the luminescence spectra by Pringsheim and Vogels,[2] clearly indicated that the absorption and luminescence are due to complex ions of the type $TlX_n^{1-n}$.

The thallium-activated alkali halide single crystal phosphors exhibit ultraviolet absorption spectra which are markedly similar to the corresponding aqueous solutions. Because of this parallel, Fromherz[3] and Hilsch[4] concluded that the absorption and luminescence of the crystal phosphors should also be attributed to complex centers within the crystal.

Evidence that thallium(I) halo complexes exist in solution is manifold. Scott and Hu[5,6] have determined the dissociation constants and molar absorptivities for TlCl and $TlCl_2^-$. Scott, Dartau, and Sapsoonthorn[7] have reported the dissociation constants and molar absorptivities for TlBr, $TlBr_2^-$, and $TlBr_4^{3-}$. Kul'ba and Mironov[8,9] indicate that TlI, $TlI_2^-$, and $TlI_4^{3-}$ exist in KI solutions containing TlI.

Recently Avramenko and Belyi[10] and Brauer and Pelte[11] have investigated the luminescence spectra KCl–TlCl and KBr–TlBr solutions. Avramenko and Belyi attributed the 430 m$\mu$ emission of the chloride solutions to TlCl and $TlCl_4^{3-}$ and the 470 m$\mu$ emission of the bromide solutions to TlBr, $TlBr_3^{2-}$, and possibly $TlBr_4^{3-}$. On the other hand, Brauer and Pelte concluded that the broad luminescence band of the chloride solutions is due to the overlap of three symmetric bands. These bands are supposedly due to $Tl^+$, TlCl, and $TlCl_2^-$ with band maxima at 368, 395, and 440 m$\mu$, respectively. They indicate that analogous results should occur in the bromide solutions; however, they did not assign a definite band to any of the bromide complexes.

## Experimental

The solutions were prepared using doubly-recrystallized analytical grade salts. The concentration of potassium halide and thallium(I) halide ranged from zero to saturation. For many of the solutions three types of spectrum were measured. Optical absorption measurements were made by means of a Beckman

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[1] H. Fromherz and K. H. Lih, *Z. physik. Chem.*, **A153**, 321 (1931).

[2] P. Pringsheim and H. Vogels, *Physica*, **7**, 225 (1940).

[3] H. Fromherz, *Z. Physik*, **68**, 233 (1931).

[4] R. Hilsch, *Proc. Phys. Soc.* (London), **49** (extra part), 40 (1937).

[5] K. H. Hu and A. B. Scott, *J. Am. Chem. Soc.*, **77**, 1380 (1955).

[6] A. B. Scott and K. H. Hu, *J. Chem. Phys.*, **23**, 1830 (1955).

[7] A. B. Scott, R. G. Dartau, and S. Sapsoonthorn, *Inorg. Chem.*, **1**, 313 (1962).

[8] F. Y. Kul'ba and V. E. Mironov, *Russ. J. Inorg. Chem.*, **2** (part 6), 78 (1957).

[9] F. Y. Kul'ba and V. E. Mironov, *ibid.*, **3** (part 6), 68 (1958).

[10] V. G. Avramenko and M. U. Belyi, *Bull. Acad. Sci. USSR, Phys. Ser.*, **24**, 737 (1960).

[11] P. Brauer and D. Pelte, *Z. Naturforsch.*, **17a**, 875 (1962).

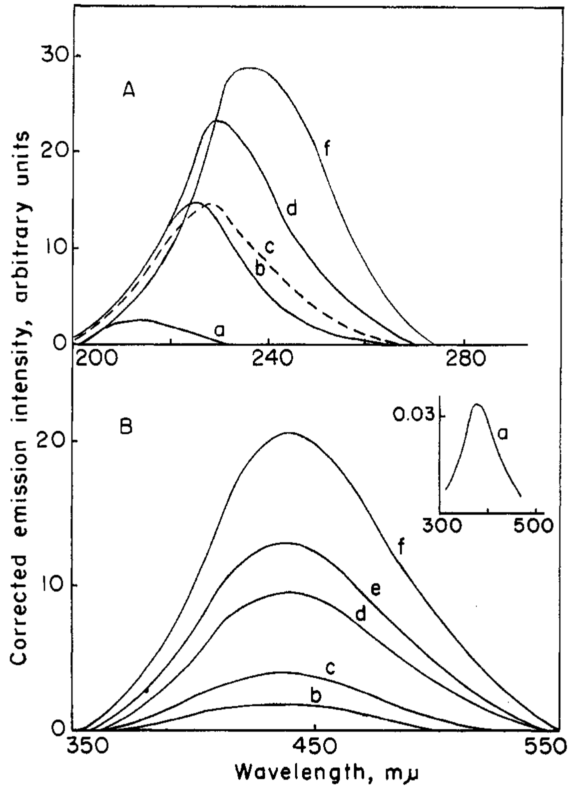

Fig. 1.—Excitation and emission spectra for KCl solutions with TlCl concentration 1.33 × $10^{-4}$ *M:* A, excitation, 430 mμ emission; B, emission, 250 mμ excitation; KCl concentration: a, 0.0; b, 0.5; c, 1.0; d, 2.0; e, 3.0; f, 4.0 *M.*

Model DU or DK-1 spectrophotometer. The luminescence excitation and emission spectra were measured using an Aminco-Bowman spectrophotofluorometer. Excitation spectra were obtained by recording the luminescence intensity at fixed wave length as a function of the wave length of the exciting source, whereas emission spectra are records of the spectral distribution of luminescence at fixed excitation wave length.

The observed emission intensity was corrected for (a) the variation of intensity of the xenon arc excitation source with wave length, (b) the absorption of exciting radiation by that portion of the solution which was between the source and the region of solution viewed by the emission monochromator, and (c) the variation of sensitivity of the photomultiplier detector with wave length. The spectral dependence of the xenon arc intensity was determined by means of a potassium oxalatoferrate actinometer.[12,13] The correction for (b) was calculated from the measured absorbance of the solutions; that for (c) was taken from the manufacturer's data. After application of the corrections, the *corrected emission intensity* is a number proportional to the power falling upon the detector for fixed power incident upon the region of solution viewed by the emission monochromator. The data given here were further corrected by subtracting the emission of very low intensity given by the KCl and KBr solutions which contained no thallium.

Presented in Fig. 1–3 are representative excitation and emission spectra of KCl–TlCl, KBr–TlBr, and KI–TlI solutions. The iodide solutions exhibit very weak luminescence compared with chloride or bromide solutions.

It was found that in each case the excitation spectrum closely paralleled the absorption spectrum. The emission spectra exhibit a similar shift of the emission peak wave length and change in peak height with increasing halide ion concentration.

Pringsheim[2] has reported the appearance of a weak ultraviolet luminescence band with maximum at 300 mμ for the chlorides and at 320 mμ for the bromides; however, no emission band in the near-ultraviolet portion of the spectrum was observed for the chlorides or bromides.

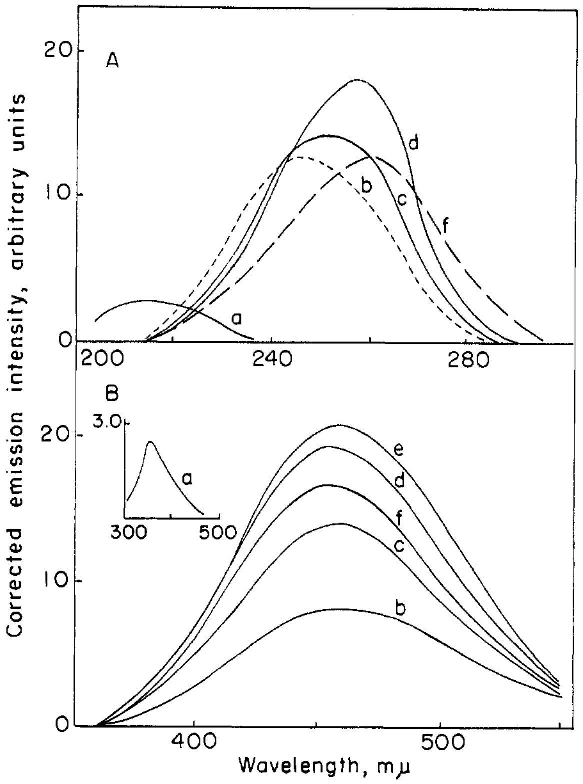

Fig. 2.—Excitation and emission spectra for KBr solutions with TlBr concentration 2.67 × $10^{-5}$ *M:* A, excitation, 470 mμ emission; B, emission, 260 mμ excitation; KBr concentration: a, 0.0; b, 0.5; c, 1.0; d, 2.0; e, 3.0; f, 4.0 *M.*

## Analysis of the Emission Spectra

The concentration of each species present in the solutions was computed using the dissociation constants for the complexes; considered were $\mathrm{Tl}^+$, TlX, $\mathrm{TlX_2}^-$, and $\mathrm{TlX_4}^{3-}$. Consider the following equilibria and dissociation constants

$$\mathrm{TlX} = \mathrm{Tl}^+ + \mathrm{X}^-;\quad K_1 = \frac{[\mathrm{Tl}^+][\mathrm{X}^-]f_\pm^{\,2}}{[\mathrm{TlX}]}$$

$$\mathrm{TlX_2}^- = \mathrm{TlX} + \mathrm{X}^-;\quad K_2 = \frac{[\mathrm{TlX}][\mathrm{X}^-]}{[\mathrm{TlX_2}^-]}$$

$$\mathrm{TlX_4}^{3-} = \mathrm{TlX_2}^- + 2\mathrm{X}^-;\quad K_{4\mathrm{c}} = \frac{[\mathrm{TlX_2}^-][\mathrm{X}^-]^2}{[\mathrm{TlX_4}^{3-}]}$$

In the above equations, $\mathrm{X}^-$ denotes a halide ion, brackets indicate concentration in moles/liter, and $f_\pm$ is the mean ionic activity coefficient. Of the above dissociation constants $K_1$ and $K_2$ are, to a first approximation, thermodynamically correct, while $K_{4\mathrm{c}}$ is concentration dependent. For singly-charged ions, $f_\pm$, taken to be that of the KCl or KBr only, was found for each solution by interpolation in the table of Harned[14] and was corrected for use with volume concentration. The values of $K_1$, $K_2$, and $K_{4\mathrm{c}}$ are 0.25, 1.87, and 93 for

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(12) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

(13) C. E. White, M. Ho, and E. Q. Weimer, *Anal. Chem.*, **33**, 438 (1960).

(14) H. S. Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).

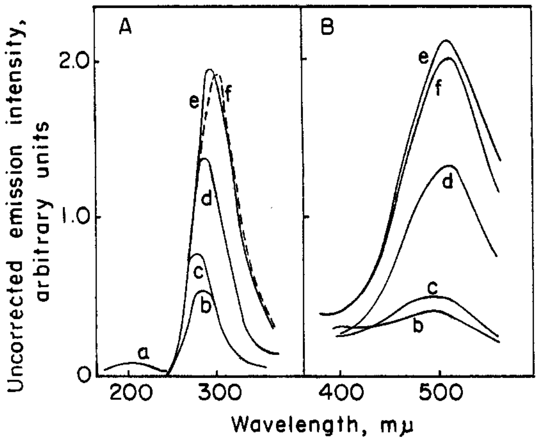

Fig. 3.—Excitation and emission spectra for KI solutions containing TlI: A, excitation, 500 mμ emission; B, emission, 300 mμ excitation; concentration of KI/concentration of TlI: a, 0.0/1.07 × $10^{-5}$; b, 0.5/1.07 × $10^{-5}$; c, 1.0/1.07 × $10^{-5}$; d, 2.0/8.05 × $10^{-5}$; e, 3.0/8.05 × $10^{-5}$; f, 4.0/8.05 × $10^{-5}$ *M*.

TlCl, $TlCl_2^-$, and $TlCl_4^{3-}$, respectively,[15] and are 0.24, 0.30, and 16 for TlBr, $TlBr_2$,$^-$ and $TlBr_4$,$^{3-}$ respectively.[7]

The emitted luminescence flux, *F*, at a given excitation and emission wave length is equal to the sum of the flux for each species, that is

$$F = F_0 + F_1 + F_2 + F_4$$

where the subscript denotes the number of halide ions coordinated with the thallium ion. At low concentrations, the luminescence flux of a species of coordination number *n* may be written as[16]

$$F_n = Ix\phi_n\epsilon_n c_n$$

where *I* is the incident flux of exciting radiation in photons per unit time, *x* is the sample thickness, $\phi$ is the quantum yield of the process, and $\epsilon$ and *c* are, respectively, the molar absorptivity and concentration of the species. Letting

$$y_n = Ix\phi_n\epsilon_n$$

then

$$F = y_0c_0 + y_1c_1 + y_2c_2 + y_4c_4$$

The above equation may be combined with the dissociation-constant equations to give

$$F = [TlX_2^-]\left(\frac{z^2}{K_{4c}}\,y_4 + y_2 + \frac{K_2}{z}y_1 + \frac{K_1K_2}{z^2f_\pm^2}\,y_0\right)$$

where *z* is the halide ion concentration. The corrected emission intensity, which will be symbolized *F'*, is actually proportional to the flux of emitted energy, whereas *F* is the flux of photons per unit time. Let

$$F' = \beta_1\beta_2F$$

where $\beta_1$ is a constant depending upon the optical geometry of the spectrophotofluorometer and $\beta_2$ is the energy per photon at a given wave length. The corrected emission intensity was plotted against $TlX_2^-$ concentration for each series of solutions of varying total thallium concentration but of constant *z* at a fixed excitation and emission wave length. The slope, equal to

$$\beta_1\beta_2\left(\frac{z^2}{K_{4c}}y_4 + y_2 + \frac{K_2}{z}\,y_1 + \frac{K_1K_2}{z^2f_\pm^2}\,y_0\right)$$

should be constant if the *y* values do not vary with concentration. Corresponding to each value of *z* is a slope, and the linear equations determined by the slopes may be solved simultaneously to obtain values for $\beta_1\beta_2y_n$. Values for $\beta_1\beta_2y_0$ were obtained from the emission spectrum of dilute TlX solutions in which association is negligible.

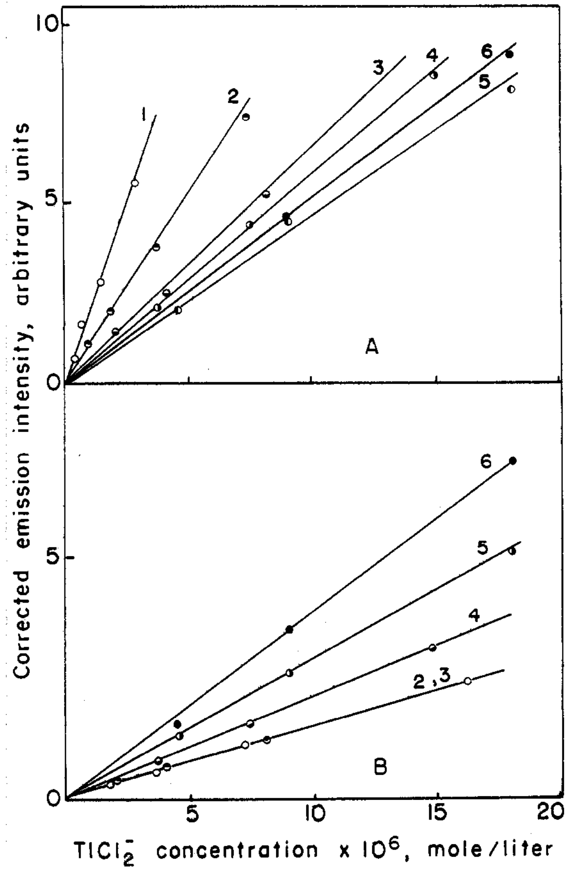

Fig. 4.—Emission at 430 mμ as a function of $TlCl_2^-$ concentration: A, 230 mμ excitation; B, 250 mμ excitation; KCl concentration: 1, 0.25; 2, 0.5; 3, 1.0; 4, 2.0; 5, 3.0; 6, 4.0 *M*. To convert to total Tl concentration for each curve, divide abscissas by the following: 1, 0.04; 2, 0.11; 3, 0.24; 4, 0.44, 5, 0.54; 6, 0.54.

Since

$$y_n = Ix\epsilon_n\phi_n$$

*I*, *x*, $\beta_1$, and $\beta_2$ all being constant, the ratio $\beta_1\beta_2y_n/\epsilon_n$ is proportional to the quantum yield, $\phi_n$.

**KCl–TlCl Solutions.**—Presented in Fig. 4 are curves of *F'* against $TlCl_2^-$ concentration for several values of chloride ion concentration with excitation at 250 mμ and emission at 430 mμ. Similar plots were prepared for excitation at 230 mμ and emission at 400, 450, and

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(15) The value of $K_{4c}$ was obtained by evaluating the solubility data of Hu and Scott at high chloride ion concentration, as outlined in ref. 5 and 7.

(16) H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," 3d Ed., D. Van Nostrand, Princeton, N. J., 1958.

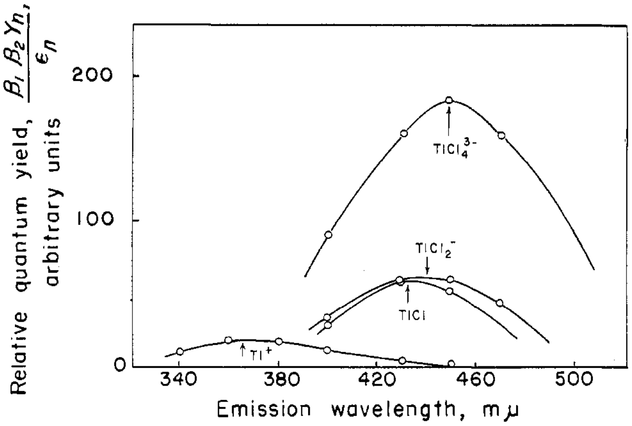

Fig. 5.—Relative quantum yields for chloro complexes.

470 mμ. The curves were nearly linear up to about $[TlCl_2^-] = 3.5 \times 10^{-5}$ *M* and passed through the origin. Values of $\beta_1 \beta_2 y_n$ were obtained as outlined above. In most cases there were more equations involving the slopes than unknowns, in which cases $\beta_1\beta_2 y_n$ values were chosen which gave the best general agreement among the equations. Results are presented in Table I.

Table I

$\beta_1\beta_2 y_n$ Values for Chloro Complexes of Thallium(I) in the Concentration Range $[TlCl_2^-] < 3.5 \times 10^{-5}$ *M*

| Emission wave length, mμ | $\beta_1\beta_2 y_n \times 10^5$, arbitrary units[a] | | | |
|---|---|---|---|---|
| | *n* | | | |
| | 0 | 1 | 2 | 4 |
| | 230 mμ excitation | | | |
| 400 | 0.15 | 1.1 | 1.8 | 2.5 |
| 430 | 0.057 | 2.3 | 2.7 | 7.0 |
| 450 | 0.028 | 2.0 | 2.6 | 9.1 |
| 470 | 0 | 1.7 | 2.3 | 8.5 |
| | 250 mμ excitation | | | |
| 400 | 0 | 0 | 1.2 | 4.3 |
| 430 | 0 | 0 | 2.1 | 7.4 |
| 450 | 0 | 0 | 2.1 | 8.9 |
| 470 | 0 | 0 | 1.6 | 7.5 |

[a] For consistency, the units of *F'* are taken to be the same as used in the figures, and concentration is in mole l.$^{-1}$

As a test of these results, the emission curve for 3.0 *M* KCl containing TlCl at a concentration of $3.33 \times 10^{-5}$ *M* under 250 mμ excitation was calculated from

$$F' = \beta_1\beta_2(y_0c_0 + y_1c_1 + y_2c_2 + y_4c_1)$$

the *c* values being given by the dissociation constants. Table II gives a comparison between the observed and calculated emission intensities at four wave lengths.

Table II

Calculated and Observed Emission Intensities, $F'^a$

| λ, mμ | Emission intensity, *F'*, arbitrary units | |
|---|---|---|
| | Calcd. | Obsd. |
| 400 | 2.88 | 2.99 |
| 430 | 5.01 | 5.11 |
| 450 | 5.26 | 5.32 |
| 470 | 4.29 | 3.85 |

[a] 3.0 *M* KCl, $3.33 \times 10^{-5}$ *M* TiCl, 250 mμ excitation.

For each complex, $\beta_1\beta_2 y_n/\epsilon_n$ was calculated using molar absorptivities, at the excitation wave length, previously given.[6,17] These values, which represent relative quantum yields, are given in Fig. 5. The data shown represent results using either 230 or 250 mμ excitation; actually, $\beta_1\beta_2 y_n/\epsilon_n$ in some cases varied considerably with the excitation wave length. However, the form of the variation with emission wave length was in all cases as shown, so that while the numerical values are at best semiquantitative, we consider the locations of band maxima to be well established by this procedure. The wave length of maximum quantum efficiency for each complex is given in Table III.

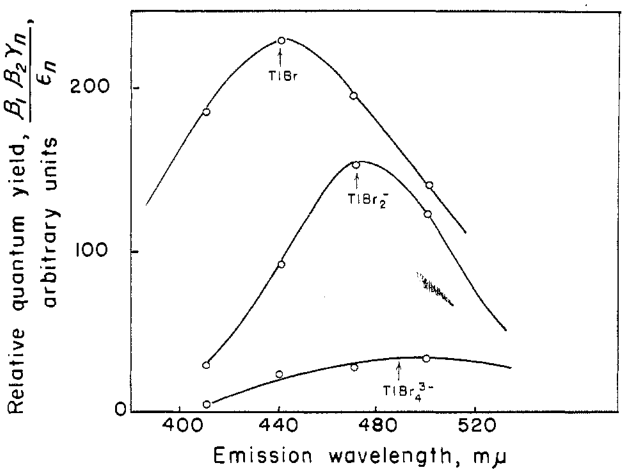

Fig. 6.—Relative quantum yields for bromo complexes.

Table III

Wave Length of the Emission Maximum of $TlX_n^{1-n}$ Complexes

| | Wave length of emission maximum, mμ | | | |
|---|---|---|---|---|
| | X = Cl$^-$ | | | |
| *n* | This work | Brauer and Pelte | Avramenko and Belyi | X = Br$^-$ |
| 0 | 370 | 368 | 380 | 370 |
| 1 | 435 | 395 | 428 | 440 |
| 2 | 435 | 440 | | 475 |
| 4 | 450 | | 428 | 495 |

**KBr–TlBr Solutions.**—Curves of *F'* against $TlBr_2^-$ concentration at *z* = 0.5, 1.0, 2.0, 3.0, and 4.0 *M* for 470 mμ emission with excitation at 240, 250, 260, and 270 mμ were drawn. Similar plots were prepared for emission at 410, 440, and 500 mμ. Results are presented in Table IV and Fig. 6. The wave length of maximum quantum efficiency is given in Table III. It is evident from Fig. 6 that the yield is greatest for TlBr and least for $TlBr_4^{3-}$. This result is in contrast to that for the chloride complexes; the reason is as yet unknown.

**KI–TlI Solutions.**—An attempt was made to obtain the molar absorptivity of complex species, but strong interference from traces of $I_3^-$, even in the presence of reducing agents, made the optical absorption data unreliable. Further the luminescence was relatively weak,

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(17) The data of ref. 6 were used in extending the calculation to include $\epsilon_4$, as was done in ref. 7 for KBr. This had the result of altering $\epsilon_2$ somewhat. The values used in the present case were (in order: λ, mμ, $\epsilon_2 \times 10^{-3}$, $\epsilon_4 \times 10^{-3}$, l. mole$^{-1}$ cm.$^{-1}$): 230, 3.1, 1.1; 250, 3.5, 4.7. Note that column headings in Table II, ref. 6, should read $\epsilon_{w,x,y} \times 10^{-3}$.

TABLE IV

$\beta_1\beta_2y_n$ VALUES FOR BROMO COMPLEXES OF THALLIUM(I)

| Emission wave length, mμ | $\beta_1\beta_2y_n \times 10^5$, arbitrary units | | | |
|---|---|---|---|---|
| | $n$ | | | |
| | 0 | 1 | 2 | 4 |
| | 250 mμ excitation | | | |
| 410 | 0 | 1.6 | 1.1 | 0 |
| 440 | 0 | 2.0 | 3.9 | 1.8 |
| 470 | 0 | 1.7 | 6.0 | 2.7 |
| 500 | 0 | 1.2 | 5.4 | 7.2 |
| | 260 mμ excitation | | | |
| 410 | 0 | 0 | 1.2 | 0.45 |
| 440 | 0 | 0 | 3.6 | 2.1 |
| 470 | 0 | 0 | 6.0 | 2.6 |
| 500 | 0 | 0 | 4.8 | 3.3 |

so that it was not considered worthwhile to analyze the emission spectra by the above method.

## Discussion

The chief difference between the present results for the chloro complexes and those of Brauer and Pelte[11] is in the location of the emission band of TlCl. Brauer and Pelte relied upon the symmetry and location of bands, under polychromatic excitation, but not upon intensities or independently-established concentrations of complex ions, to deduce characteristic emission curves. In establishing the emission curve for TlCl, for example, a curve characteristic of saturated KCl–TlCl solution was subtracted, after multiplication by an adjustable factor in the neighborhood of 0.6 chosen to leave a symmetric residue, from the emission curve of a solution 0.049 $M$ with respect to KCl and $5.6 \times 10^{-3}$ $M$ with respect to TlCl. The curve for the saturated KCl–TlCl solution was taken to represent the emission of $TlCl_2^-$ alone; however, such a solution, under the excitation used, would, according to the present results, display a large emission component arising from $TlCl_4^{3-}$. Further, in the more dilute solution, whose emission was ascribed about equally to TlCl and $TlCl_2^-$, the concentration of TlCl, calculated from the dissociation constants, is more than 30 times the concentration of $TlCl_2^-$, so that it appears that the emission may have been primarily that of TlCl, even though the excitation source was filtered to reduce the intensity of light of $\lambda < 250$ mμ.

No quantitative comparison can be made between the two experiments, since the concentration range used by Brauer and Pelte lies outside of the range of validity of the $\beta_1\beta_2y_n$ values reported here; further, their excitation sources were not monochromatic.

Two assumptions made here in analyzing the emission spectra should be borne in mind. The dissociation constants were assumed to be independent of concentration; further, the concentration of species for which $n$ was other than 0, 1, 2, or 4 was assumed zero. While $K_1$ and $K_2$ should be constant to a first approximation, the activity coefficients for $X^-$ and $TlX_2^-$ approximately canceling in $K_2$, $K_{4c}$ is expected to vary in an unknown way. The effect on the results of Fig. 5 cannot at present be assessed. In the chloride solutions $K_{4c}$ is sufficiently large that only at KCl concentrations above 3 $M$ does the calculated concentration of $TlCl_4^{3-}$ become appreciable (5% of the total thallium concentration at 3 $M$, 9% at 4 $M$), so that the effect on the results for $n = 1$ and 2 is not serious. On the other hand, the corresponding calculated relative concentrations for $TlBr_4^{3-}$ in 3 and 4 $M$ KBr are 33 and 48%, so that the effect of variation of $K_{4c}$ is likely to be considerable.

The complete absence, at high halide ion concentration, of complexes such as $TlX_3^{2-}$ has not been established. We rely here upon solubility and absorption data[5-7] which have been satisfactorily analyzed assuming $n$ to take on values of 0, 1, 2, and 4 only. While this procedure does not definitely preclude the existence of $TlX_3^{2-}$ complexes, it is clear that the corresponding dissociation constant must be large.

The failure of the curves such as those of Fig. 4 to remain linear at the higher concentrations should be remarked. Only the lower concentration range is shown in the figure; at concentrations of $TlCl_2^-$ above about $3.5 \times 10^{-5}$, a marked decrease in slope generally occurred. This may result in part from variation of the dissociation constant with concentration, or neglect of the presence of complexes such as $TlX_3^{2-}$, but in addition a quenching of the luminescence due to interaction between complex centers may be responsible.

**Acknowledgment.**—The assistance of Professors V. H. Freed and Clara Storvick, who made available the equipment used in this study, is gratefully acknowledged.