[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Relationships among the Ultraviolet Absorption Spectra of the 8-Quinolinol Chelates of the Group III-B Elements

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Although the characteristic bands in the absorption spectra of the 8-quinolinol chelates in chloroform have been of considerable use in the colorimetric determination of aluminum,[2,3,4,5] gallium,[6] indium[7] and thallium,[6] no attempt has been made to compare these spectra rigidly nor to point out any relationships which exist among them. Inasmuch as chelates of the tripositive ions are all of the type $M(C_9H_6ON)_3$, their spectra would be expected to be similar except for small displacements in the bands resulting from alterations in the size and mass of the central "ion." Furthermore, spectra of these materials would be expected to resemble that of 8-quinolinol, except possibly for wave-length shifts because in these compounds the metal ions play the same role as does the acidic hydrogen in the parent compound. Such relationships have been verified.

Experimental

Materials Used.—Gallium and indium compounds were prepared from samples of the metals which contained only spectroscopic traces of other materials. Thallium compounds were prepared from chemically pure samples of thallium(III) oxide and thallium(I) sulfate. The 8-quinolinol used was an Eastman Kodak Co. product. Chloroform employed contained 0.75% ethanol by volume as a preservative. All other chemicals were of analytical reagent quality and were used without further purification.

Preparation of 8-Quinolinol Chelates.—The 8-quinolinol chelates of aluminum, gallium, indium, and thallium(III) were prepared by precipitation from acetate-buffered solutions at previously determined optimum temperatures.[2,6,7] The thallium(I) chelate was obtained by a modification[6] of Rey's procedure.[8] All compounds were shown to be pure by analysis. Solutions studied were prepared by dissolving weighed quantities of the chelates in chloroform and diluting to predetermined volumes.

Absorption Spectra Measurements.—Absorption spectra were measured by means of an unmodified Beckman Model DU Quartz Spectrophotometer, using 5.0-cm. demountable cells with quartz windows. Optical density readings were made at 5 mμ intervals, using chloroform solutions of 8-quinolinol and the various chelates with chloroform as the reference liquid. Molecular extinction coefficients were evaluated by use of the familiar relation $\epsilon = (M/cl) \log_{10} (I_0/I)$ and equivalent extinction coefficients by dividing the molecular values by the appropriate oxidation numbers. Concentrations (c) of 8-quinolinol solutions were expressed in grams of solute per liter; those of chelate solutions in grams of metal per liter.

Results and Discussion

Absorption Spectrum of 8-Quinolinol.—The absorption spectrum of 8-quinolinol in chloroform is exactly similar to that reported for the compound in 95% ethanol[9] except that absorption peaks center at 251 mμ and 318 mμ while in ethanol these peaks are found at *ca.* 245 mμ and 320 mμ. Corresponding bands at 250 mμ and 320 mμ are found in carbon tetrachloride and in cyclohexane.[10] The molecular extinction coefficient of 2.31×10^3 characterizing the 318 mμ band agrees with values of *ca.* 2.3×10^3 and 2.4×10^3 found for ethanol[9] and cyclohexane[10] solution. Although the 318 mμ peak shifts to slightly longer wave lengths with increasing concentration, Beer's law is obeyed. Chloroform solutions of 8-quinolinol are stable indefinitely in the absence of strong sunlight.

Absorption Spectra of 8-Quinolinol Chelates of the Tripositive Group III-B Elements.—In the wave length range 249–800 mμ, chloroform solutions of these compounds all exhibit four distinct absorption bands. The intense bands in the region 250–275 mμ, corresponding to shifts in the 251 mμ band of 8-quinolinol, were not investigated because of the limitations of the instrument at the concentrations under general study. The other three bands, however, were investigated in some detail. As shown in Fig. 1, where data for aluminum, gallium, indium, and thallium(III) compounds at roughly equivalent concentrations are plotted, the spectra are nearly identical except for displacements of the bands to longer wave lengths with increasing equivalent weight and size of the central metal "ion." Numerical data characterizing these spectra are summarized in Table I.

It is apparent that regardless of the metal present the equivalent extinction coefficients at the 390–401 mμ absorption peaks are the same, the average for the four compounds being 2.22×10^3. Agreement between these values and the molecular extinction coefficient for 8-quinolinol at 318 mμ suggests that the absorption bands of the chelates in this region result from bathochromic shifts of the 318 mμ 8-quinolinol band. Although the exact amount of the wave-length shift depends upon the equivalent weight and size of the metal "ion" present, the quantity of energy absorbed is determined only by the amount of organic material present in the compound. Even a large difference in equivalent weight appears to produce only slight wave length differences among the compounds since, for example, the thallium(III) peak is only 10 mμ removed from that for aluminum. Chelation to the metal ion, therefore, rather than the nature of the metal "ion" is primarily responsible for the observed

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[2] Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 346 (1943).

[3] Gentry and Sherrington, *Analyst*, **71**, 432 (1946).

[4] Parks and Lykken, *Anal. Chem.*, **20**, 1102 (1948).

[5] Wiberly and Bassett, *ibid.*, **21**, 609 (1949).

[6] Moeller and Cohen, *ibid.*, **22**, 686 (1950).

[7] Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 270 (1943).

[8] Rey, *Ion*, **7**, 389 (1947).

[9] Ewing and Steck, THIS JOURNAL, **68**, 2181 (1946).

[10] Phillips and Merritt, *ibid.*, **71**, 3984 (1949).

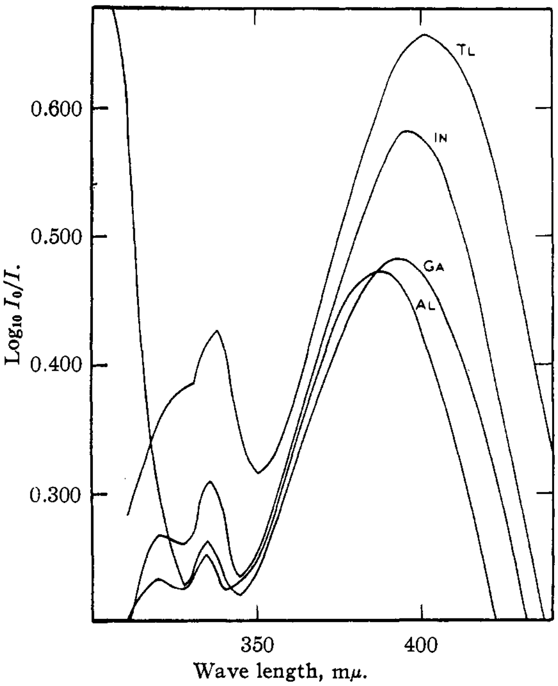

Fig. 1.—Absorption spectra of the 8-quinolinol chelates of the tripositive elements in chloroform, concentrations in mg. of metal per liter: Al, 0.4; Ga, 1.0; In, 2.0; Tl, 4.0.

bathochromic shifts. Similar shifts are reported for chelates of the dipositive metals.[10]

TABLE I

ABSORPTION SPECTRA DATA FOR 8-QUINOLINOL CHELATES

Chelate	Ionic radius,[a] Å.	Absorption peak, mμ	Molecular extinction coefficient[b] ($\times 10^{-3}$)	Equivalent extinction coefficient[b] ($\times 10^{-3}$)
$Al(C_9H_6NO)_3$	0.50	303	10.9	3.63
		334	3.38	1.12
		390	6.61	2.20[c]
$Ga(C_9H_6NO)_3$	0.62	320	3.34	1.11
		335	3.67	1.22
		392.5	6.47	2.16[c]
$In(C_9H_6NO)_3$	0.81	320	3.08	1.03
		336	3.58	1.19
		395	6.67	2.22[c]
$Tl(C_9H_6NO)_3$	0.95	328	4.20	1.40
		338	4.62	1.54
		401	6.79	2.26[c]
TlC_9H_6NO	1.15	310	1.96	1.96
		325	1.92	1.92
		338	1.93	1.93
		395	2.27	2.27[c]

[a] Listed only for rough comparisons since all compounds are covalent. Covalent radii permitting strict comparisons are inexactly known. [b] Calculated for 5.0 cm. light path, using logarithms to base 10. [c] Average 2.22×10^3 for peaks at 390–401 mμ.

The other absorption maxima appearing in the range 303–338 mμ are apparently characteristic of these chelates but cannot be related as precisely to the spectrum of the parent compound. Although adherence of absorption at these peaks to Beer's law is less rigid than at the 390–401 mμ peaks, detailed studies with the gallium chelate have shown fairly close dependence on the relation.[6] It is interesting that the equivalent extinction coefficient of the gallium compound at 320 mμ is exactly half that of 8-quinolinol at 318 mμ.

The absorption spectra of the 5,7-dibromo-8-quinolinol chelates of aluminum and gallium[11] are exactly similar to those of the corresponding 8-quinolinol chelates except for further bathochromic shifts and increases in equivalent extinction coefficients at the absorption peaks. For example, the molecular extinction coefficient at 328 mμ for 5,7-dibromo-8-quinolinol is 2.95×10^3, while equivalent extinction coefficients of 2.88×10^3 and 2.95×10^3 are noted at 405 mμ and 409 mμ for the aluminum and gallium chelates, respectively.

Chloroform solutions of the 8-quinolinol chelates are light sensitive.[6] Photochemical decomposition is characterized by a decrease in the height of the absorption in the region 390–401 mμ and the appearance of a peak in the region 315–318 mμ. This is shown in Fig. 2 where data obtained for a given gallium chelate solution immediately after its preparation (20 min.) are compared with those obtained after exposure to sunlight for varying periods. The rate of decomposition increases as the equivalent weight and size of the central metal "ion" increase as shown by the data in Fig. 3. These values are to be compared with those given in Fig. 1 for protected solutions of the same concentrations. The natures and kinetics of these photochemical decompositions have not been fully characterized. Products are formed containing the metals in question, which are insoluble in water, ethanol, benzene, acetone and ethyl ether but which dissolve in quinoline. Lack of complete agreement in equivalent extinction coefficient values for the different chelates in the

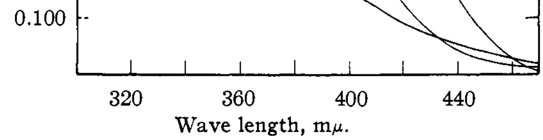

Fig. 2.—Photochemical decomposition of chloroform solution of the gallium chelate: concentration, 1 mg. Ga per liter.

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(11) Moeller and Cohen, *Anal. Chim. Acta*, **4**, in press (1950).

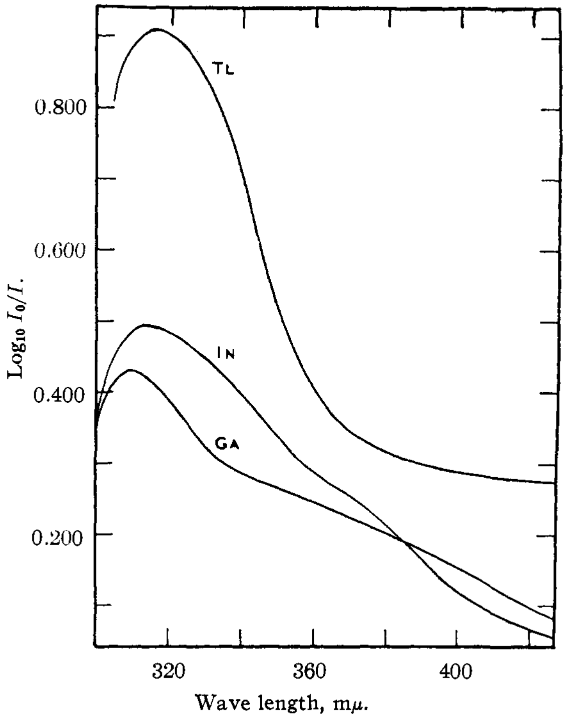

Fig. 3.—Comparison of photochemical decompositions of chloroform solutions of gallium, indium and thallium chelates: curve, Ga, 1.0 mg. Ga per liter, 7 months; In, 2.0 mg. In per liter, 6 months; Tl, 4.0 mg. Tl per liter, 4 hours.

300–340 mμ region is probably due to interferences by the absorption bands of the decomposition products which constantly increase in magnitude. Photochemical decomposition may be prevented by preparing solutions under red light and keeping them either under red light or in darkness.

Absorption Spectrum of the 8-Quinolinol Chelate of Thallium(I).—The absorption spectrum of a chloroform solution of this compound is given in Fig. 4. Apparent similarities between this spectrum and those of the tripositive materials are summarized in Table I. The equivalent extinction coefficient of 2.27×10^3 at 395 mμ together with the difference of only 6 mμ in the position of this band between the thallium(I) and thallium(III) compounds gives further support to the conclusions drawn above.

The extreme thermal and photochemical sensitivities of this compound apparent in Fig. 4 require preparation of solutions at low temperatures under very diffuse red light and limit the utilities of absorption spectra measurements.[6] Values given in Table I are for an undecomposed solution measured as soon as possible after its preparation. Photochemical decomposition is accompanied by changes from clear yellow through cloudy red, brown, green and bright blue to pale yellow with the deposition of a white solid. The true natures of these transformations have not been established.

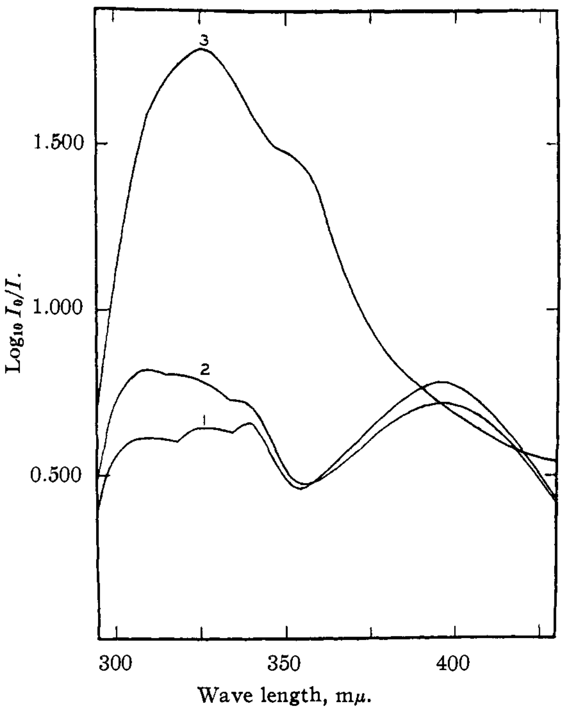

Fig. 4.—Absorption spectra of chloroform solutions of thallium(I) chelate: curve 1, 14 mg. Tl per liter, measured 7–27 minutes after preparation; curve 2, same solution, measured 99–119 minutes after preparation after storage in dark at room temperature; curve 3, same solution as in 1 measured after 195 minutes in dark plus five minutes exposure to 100-watt Mazda No. AB4 mercury vapor lamp.

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Summary

1. The absorption spectra of chloroform solutions of the 8-quinolinol chelates of aluminum, gallium, indium and thallium(I and III) have been observed in the wave length range 300–800 mμ.
2. In this range, three absorption peaks characterize all the absorption spectra.
3. Absorption peaks in the 390–401 mμ region have the same equivalent extinction coefficients as does the 318 mμ peak of 8-quinolinol and appear to be due to bathochromic shifts of this peak as a result of chelate formation.
4. The wave lengths of the various absorption bands increase with increasing equivalent weight and size of the metal "ion."
5. The photochemical stabilities of such solutions decrease with increasing size of the central metal "ion" in the chelate present.

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