Composition, Formation, And Luminescence Of Thorium(iv) 8-quinolinol And Ruthenium-imine Chelates.

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COMPOSITION, FORMATION, AND LUMINESCENCE OF THORIUM (IV)-8-QUINOLINOL AND RUTHENIUM-IMINE CHELATES

by

Gordon M. White

A Dissertation
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Gordon M. White

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DEDICATION

To "The Oscar"

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ABSTRACT

The luminescence of tetrakis-(8-quinolinolato)-thorium (IV) and several 1,10-phenanthroline ruthenium(II)-chelates was investigated.

Luminescence data may be used to supplement data obtained by more conventional methods - *e.g.*, spectrophotometry, potentiometry, in studying metal chelates and their reactions. The luminescence data may be most useful in revealing important information regarding the structure and other properties of the luminescent species that may not otherwise be easily obtained.

The orange thorium(IV)-8-quinolinol material precipitated from slightly acidic aqueous solution is shown to be a non-stoichiometric mixture of tetrakis-(8-quinolinolato)thorium (IV), ThQ_4, and 8-quinolinol, HQ, with the approximate composition $ThQ_4 . 0.6HQ$; previously the 1:1 adduct, $ThQ_4 . HQ$, had been the accepted composition.

The near-ultraviolet absorption spectrum of absolute ethanol solutions of the 4:1 chelate, ThQ_4, indicate that the compound is unstable in solution and extensive dissociation occurs. Its fourth step-wise formation constant, K_4, is approximately 10^{10}.

The effect of ligand field strength on charge transfer luminescence of several bis-(1,10-phenanthroline)-ruthenium (II) chelates was investigated. The luminescence (or lack

thereof) from these chelates appears related directly to the strength of the ligand field. The luminescence intensity of those complexes which are luminescent in fluid solution is very sensitive to the sample temperature. These observations are explained in terms of excited state spin crossover between the low- and high-spin charge transfer excited state configurations (π^*, t_{2g}^5) and (π^*, $e_g^2t_{2g}^3$).

Investigation of the formation of tris-(1,10-phenanthroline)-ruthenium(II) when a solution of Ru(III) and 1,10-phenanthroline are heated together at pH2 suggests the first species formed are bridged diols. The rate of appearance of the final product, $[Ru(II)(phen)_3]^{2+}$, is equal to the rate of appearance of ruthenium(II)-phen species. However, the nature of the intermediate steps are not known for certain and the several possibilities are discussed on the basis of available data.

I. INTRODUCTION

A. UV-Visible Luminescence

Extensive comprehensive surveys of luminescence theory are readily available in several recent books (1-3). Only a brief summary of the more important aspects pertinent to the present work is given here.

Luminescence is a process in which uv-visible radiation is emitted by molecules that have been raised to an excited electronic state. Excitation is usually accomplished by exposing the molecule in dilute solution to radiation of suitable energy to effect an electronic transition. The absorption transition occurs very rapidly - in ca. 10^{-15} sec. Nearly all molecules in a solution at room temperature are in the lowest vibrational level of the ground electronic state. Absorption therefore occurs from the zeroth vibrational level of the ground electronic state to several of the many vibrational levels within an excited electronic state.

In dilute solution the vibrationally excited molecule quickly loses its excess vibrational energy - usually by transfer to the solvent during collisions with surrounding solvent molecules. This process, known as vibrational relaxation, is complete in 10^{-13} to 10^{-11} sec, which is several orders of magnitude shorter than the lifetime of a spin-allowed excited (singlet) electronic state: approximately

10^{-9} to 10^{-7} sec. Thus, before the excited molecule can emit a photon, it will undergo vibrational relaxation to the lowest vibrational level of the excited (singlet) state having lowest energy. If a molecule in the lowest vibrational level of an excited (singlet) state emits a photon and returns to the ground state, this process is fluorescence; no afterglow is perceptible - i.e., luminescence will persist for only ca. 10 ns. after removing the excitation energy source.

Emission may take the molecule to one of several vibrational levels of the ground state; nonradiative relaxation to the lowest vibrational level of the ground state follows quickly. The loss of excitation energy to the solvent causes the fluorescence emission spectrum to appear at longer wavelengths than the absorption spectrum - usually by several thousand cm^{-1}.

If every molecule in the excited state emitted its excitation energy as fluorescence, the fluorescence quantum yield would be unity; the fluorescence quantum yield is the fraction of excited molecules that fluoresce. There are, however, processes that compete with fluorescence for the excitation energy and tend to lower the fluorescence quantum yield.

One such process is internal conversion. Although details are poorly understood, this is a radiationless process whereby molecules in an excited state may return to a lower energy state of the same multiplicity - e.g., from an excited singlet to the ground state, without the emission of a photon by converting all of the excitation energy into heat. The rate of internal conversion is inversely proportional to the energy difference between the combining states. Although internal conversion is an important process among excited states of the same multiplicity, it is generally believed negligible for the loss of excitation energy between excited singlet states and the ground state in most molecules. Internal conversion is very efficient in cases where there is extensive overlap of vibrational levels of several electronic states - e.g., among excited singlet states. Thus, regardless of the singlet state to which the molecule is excited, it will undergo vibrational relaxation and internal conversion rapidly relative to the rate of photon emission. Therefore, the luminescence spectrum of a molecule is almost always independent of the wavelength of the exciting light.

Only spin-allowed excited states of a molecule have been considered thus far - i.e., singlet states for most molecules. The extent of populating the triplet state by direct absorption from the ground singlet state is almost insignificant because it would require a spin-forbidden transition: $\Delta M \neq 0$. However, it is possible to populate the triplet states by a process called intersystem crossing. This process often involves vibrational coupling between the lowest excited singlet state and a triplet state (4,5).

Intersystem crossing is often rapid enough to compete with the fluorescence process and provides an effective means of quenching the fluorescence as well as populating the triplet state. If the rate of intersystem crossing is fast enough, the singlet state may be completely depopulated in favor of the triplet state and no fluorescence will be observed. The intersystem crossing rate is enhanced by the presence of heavy atoms and especially by paramagnetic species*.

The effect of diamagnetic species containing heavy atoms is to increase the spin-orbit coupling which in turn increases the probability of intersystem crossing. Hoijtink has attributed this effect of paramagnetic species to an exchange interaction between the excited and the paramagnetic species (6); Murrell and others considered mixing of the singlets and triplets with charge-transfer states involving the paramagnetic species (7,8). Thus, paramagnetic species are usually nonfluorescent, and, moreover, may also be very efficient quenchers of the luminescence of other species, e.g., O_2 and NO.

The triplet state is usually long-lived, ca. 10^{-4} to 10 sec., because the emission of a photon and return to the ground state, referred to as phosphorescence, is a spin-forbidden (triplet → singlet) transition. When working with

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*internal and external to excited species.

fluid solutions this long lifetime allows the excited molecule to sustain many encounters with other molecules and, thus, undergo collisional deactivation. This kind of radiationless transfer of energy is so effective and important that phosphorescence is normally observed only from molecules excited in a rigid matrix.

Figure 1 summarizes the various processes that have been described. Radiative processes are illustrated by straight lines, nonradiative processes by wavy lines. The observed luminescence behavior of a molecule depends upon the relative rate of these processes under the conditions of the experiment.

Figure 1

Summary of Processes for Excited Molecules

S_0 - ground state

S_1^* - lowest excited singlet state

S_2^* - second excited singlet state

T_1^* - lowest triplet state

A - absorption

VR - vibrational relaxation

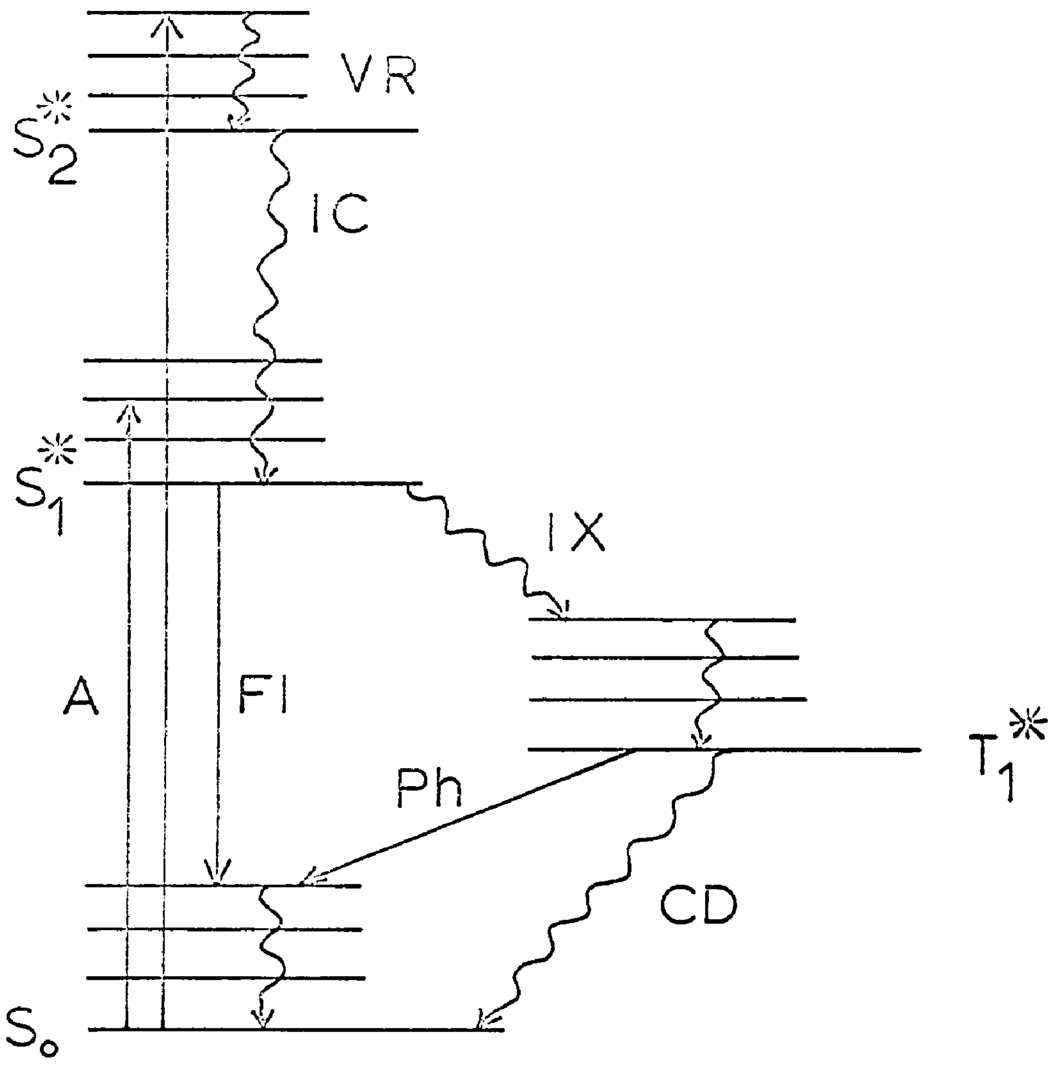
IC - internal conversion

IX - intersystem crossing

Fl - fluorescence

Ph - phosphorescence

CD - collisional deactivation


VR
S_2^*
IC
S_1^*
IX
A
Fl
Ph
T_1^*
CD
S_o

B. Luminescence of Metal Chelate Compounds

Many metal ions, while nonluminescent in themselves in solution, may be made to luminesce by forming a metal chelate. The chelating ligand usually has π bonding, thus providing loosely-held (π) electrons and vacant low energy (antibonding, π^*) orbitals for excitation ($\pi^* \leftarrow \pi$) without photodecomposition.

To a first approximation the ligand and metal ion each has its own set of energy levels. Within this approximation four different and distinct kinds of luminescence emission may occur:

1. ($\pi^* \rightarrow \pi$): radiative transition localized on the ligand.
2. ($\pi^* \rightarrow m$): ligand-to-metal charge-transfer.
3. ($m^* \rightarrow \pi$): metal-to-ligand charge-transfer.
4. ($m^* \rightarrow m$): transition between atomic orbitals of the metal ion.

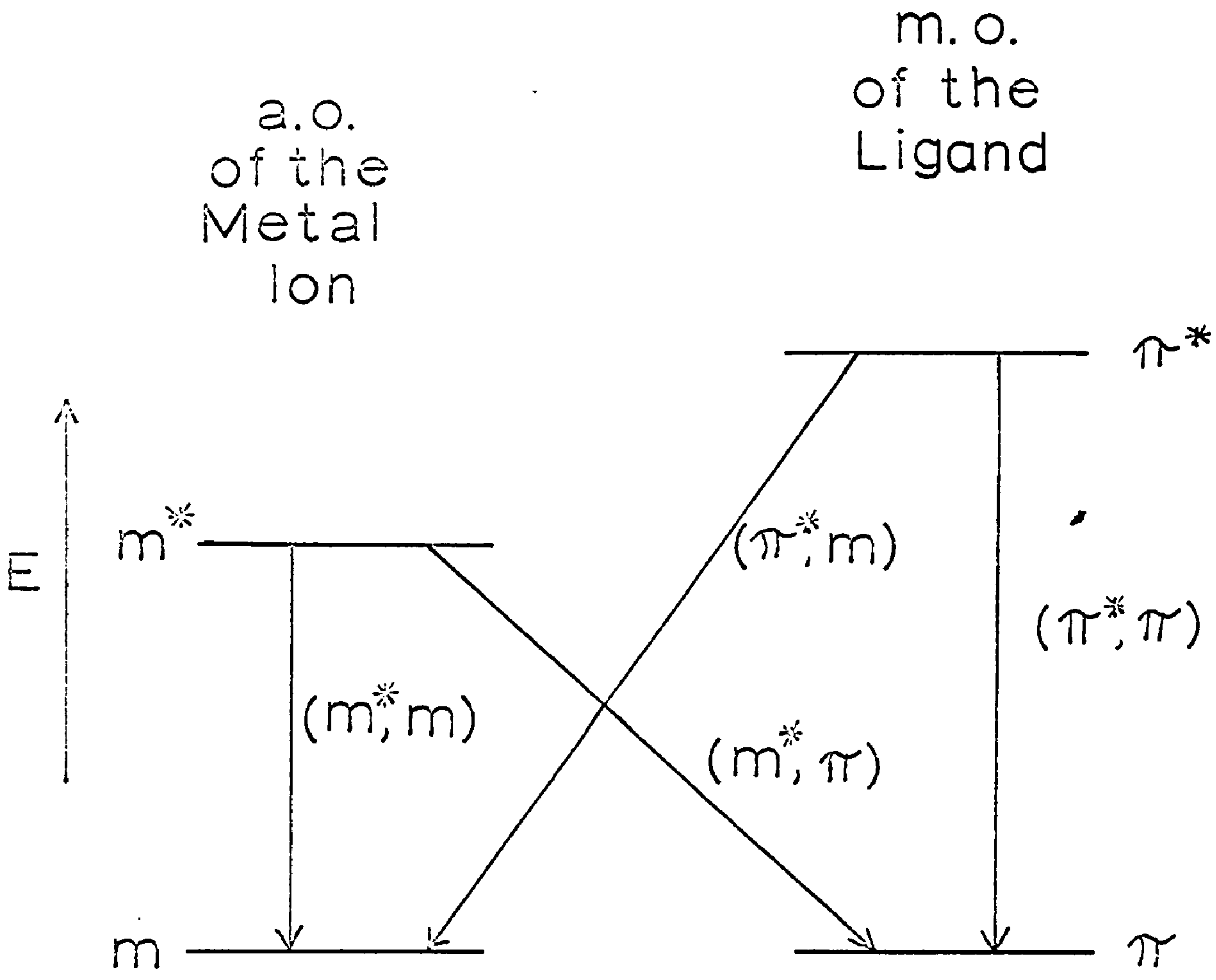
These transitions are illustrated in Figure 2.

1. $\pi^* \rightarrow \pi$ Fluorescence of Metal Chelates

Most fluorescent metal chelates exhibit $\pi^* \rightarrow \pi$ type fluorescence. Because of the nature of the combining states, the emission spectrum (at room temperature) will consist of

Figure 2

Orbital and Energy Level Diagram for a Metal Chelate


a.o.
of the
Metal
Ion
m. o.
of the
Ligand
E
m*
m
π*
π
(m*, m)
(π*, m)
(m*, π)
(π*, π)

a rather broad band showing little or no vibrational structure. Because this transition is located almost entirely on the ligand, the metal ion has little influence on the _position_ of the absorption and emission bands and on the _intensity_ of the spin-allowed $\pi^* \leftarrow \pi$ absorption (per chelated ligand species). The metal ion does, however, have a marked effect on the _intensity_ of luminescence because the metal ion affects the efficiency of the various pathways available for dissipating the excitation energy of the chelate. The primary factor is probably the effect of the metal ion on the intersystem crossing rate. When diamagnetic chelates of heavier metal ions of several ligands were examined, the fluorescence intensity was lower and in some cases the intensity of phosphorescence was enhanced compared to their counterparts with the lighter metals of the same ligands (9-11).

Paramagnetic complexes do not fluoresce because of the very high intersystem crossing rate. Thus, most transition metal ion chelates are paramagnetic and nonfluorescent due to the unpaired electron spins in the partly-filled outer d-subshell.

2. $\pi^* \rightarrow m$ Charge Transfer Luminescence of Metal Chelates

A $\pi^* \rightarrow m$ type of emission yields a spectrum which is usually somewhat narrower than the typically broad $\pi^* \rightarrow \pi$ luminescence band because one of the combining orbitals involved in the radiative transition is localized on the metal ion. As the name implies there is a transfer of an electron from an excited orbital largely localized among the ligands to an atomic orbital confined mostly to the metal ion.

Among the first reports of charge transfer luminescence were those by Paris and Brandt which described the red-orange luminescence from some Ru(II)-complexes (12,13). They described absorption and luminescence spectra of tris-2,2'-bipyridine-ruthenium(II) and several other Ru(II)-imine complexes in fluid solutions. Ruthenium(II) is a d^6 metal ion and in the presence of strong octahedral ligand fields, such as those provided by six coordinated nitrogen atoms, it assumes the diamagnetic, low-spin configuration, t_{2g}^6. The charge transfer emission was assigned on the basis of the visible absorption band intensities, their position, and their broadness: The visible absorption band is broad which suggests involvement of ligand levels (π^*). Paris and Brandt called the emission "line-like", indicating the involvement of metal ion d orbitals in the luminescent transition. The $\pi^* \rightarrow \pi$ assignment was eliminated by comparing the absorption spectrum of the chelate with that of the diprotonated form of the ligand. The latter exhibits electronic properties in the uv (below 320 nm) similar to those found in the coordinated compound thereby locating the $\pi^* \leftarrow \pi$ bands which are far removed in energy from the red-orange luminescence. Any $d^* \leftarrow d$ absorption would appear at sufficiently high energies to lie under the intense uv $\pi^* \leftarrow \pi$ ligand bands; in addition, bands due to $d^* \leftarrow d$ transitions seldom have molar absorptivities which are greater than 100. Because the visible absorption bands under consideration have $\epsilon > 10^3$, they are definitely "allowed" transitions. Transitions of the type $d^* \leftarrow \pi$ are excluded on the basis of the high energy that would be necessary to effect this transition. In his thesis Paris (13) assigned the charge transfer luminescence of tris-2,2'-bipyridineruthenium(II) as phosphorescence, $({}^3\pi^* \rightarrow d)$ based on the fact he found no evidence of any other emission at low temperature in solid solution, i.e., phosphorescence, than was observed in solution at room temperature. Since the presence of the heavy ruthenium ion would promote singlet-triplet intersystem crossing,Paris reasoned that the luminescence he observed at low temperatures was phosphorescence and thus, that same luminescence which he observed at room temperature in liquid solution must also be phosphorescence. In a note describing the same work Paris and Brandt referred to the luminescence as fluorescence, $({}^1\pi^* \rightarrow d)$, rather than phosphorescence although they made no specific mention of the assignment of the multiplicity of the emitting π state as a singlet (12).

In 1964 and 1965 Porter (14), Crosby (15), and their coworkers proposed reassigning the luminescence of tris(2,2'-bipyridine)- and tris(1,10-phenanthroline)-ruthenium(II) as ligand field $(d^* \rightarrow d)$ fluorescence $t_{2g}^5 e_g^1 \rightarrow t_{2g}^6$, $({}^1T_1 \rightarrow {}^1A_1)$. They reported the mean lifetime of the emitting state in rigid alcohol solution as 6μ sec for the bipyridine chelate and 10μ sec for the 1,10-phenanthroline-ruthenium(II) species. These authors did agree that the intense (ε ca. 10^4) visible absorption band near 450 nm was a $\pi^* \leftarrow d$ charge transfer band, but they also uncovered two weak transitions on the red tail of the charge transfer absorption band, at 18,550 cm^{-1} and at 15,050 cm^{-1}, for tris(2,2'-bipyridine)-ruthenium(II). Based upon the assignment of these latter transitions as $d^* \leftarrow d$ bands (${}^1T_1 \leftarrow {}^1A_1$ and ${}^3T_1 \leftarrow {}^1A_1$ respectively) at lower energy than the charge transfer absorption band, they proposed to reassign the luminescence to a ligand field transition ${}^1T_1 \rightarrow {}^1A_1$. The 1,10-phenanthroline complex luminescence was assigned in an analogous manner although no absorption bands due to the ${}^3T_1 \leftarrow {}^1A_1$ or ${}^1T_1 \leftarrow {}^1A_1$ transitions were observed.

Mercer and Buckley (16) observed two bands in the absorption spectrum of $Ru(H_2O)_6^{+2+}$ which they assigned as $d^* \leftarrow d$ transitions, the band at 25,640 cm^{-1} (390 nm) was assigned to the ${}^1T_2 \leftarrow {}^1A_1$ transition and that at 18,870 cm^{-1} (530 nm) to ${}^1T_1 \leftarrow {}^1A_1$. On this basis - because N-donors give much stronger ligand fields, Paris's assumption that $d^* \leftarrow d$ for Ru(II) imines would be at considerably higher energy than the visible charge transfer $\pi^* \leftarrow d$ was experimentally justified. Crosby (23) later acknowledged that the band they saw at 15,050 cm^{-1} was due to some impurity (probably the Ru(III)-imine). Palmer and Piper concluded that, based on the spectrum of $Ru(H_2O)_6^{+2+}$ and the high extinction coefficient of the 18,500 cm^{-1} band, there is no reason to assign it to a d-d transition (17).

In a later publication Crosby (18) first assigned the low temperature emission from rigid solutions containing (2,2',2''-terpyridine) ruthenium(II) and transition metal ion complexes of some other d^6 metal ions as $d^* \rightarrow d$ fluorescence: -*e.g.*, hexacyanocobalt(III), (2,2',2''-terpyridine) osmium(II), and (1,10-phenanthroline)iridium(III). In a note added in proof in this same paper Crosby reassigned the luminescence from Ru(II)-imine complexes as charge transfer in origin and suggested a reassignment of the transitions reported for the Os(II) and Ir(III) complexes to charge transfer emissions.

Wunschel and Ohnesorge (19) assigned the emission from *tris*-(2,2'-bipyridine)-iridium(III) and *tris*-(1,10-phenanthroline)-iridium(III) chelates as charge transfer $(\pi^* \rightarrow d)$ luminescence based upon spectroscopic evidence and energy considerations applied to similar Ir(III) systems studied by Jorgensen (20).

Jorgensen attributed bands in the range 285-345 nm in the absorption spectra of 20 Ir(III)-pyridine complexes to $(\pi^* \leftarrow d)$ charge transfer transitions (20). Spectral studies of the *tris*-(ethylenediamine)-iridium(III) ion, $[Ir(en)_3]^{+3+}$, in solution show the lowest energy singlet

$d^* \leftarrow d$ ($^1T_1 \leftarrow {}^1A_1$) transition at 249 nm and the lowest energy triplet ($^3T_1 \leftarrow {}^1A_1$) transition at 302 nm (21). Both 2,2'-bipyridine and 1,10-phenanthroline are placed above ethylenediamine in the spectrochemical series (22). Therefore, in $[Ir(bipy)_3]^{3+}$ and $[Ir(phen)_3]^{3+}$ the splitting of the several ligand field states will be larger than in $[Ir(en)_3]^{3+}$, and more energy will be required to effect the $^1T_1 \leftarrow {}^1A_1$ and $^3T_1 \leftarrow {}^1A_1$ transitions. The energy required for a ligand-field transition in the 2,2'-bipyridine and 1,10-phenanthroline chelates of Ir(III) is estimated as approximately equal to the energy necessary for an intraligand ($\pi^* \leftarrow \pi$) transition and thus is greater than that for a charge-transfer ($\pi^* \leftarrow d$) transition. The luminescence of these Ir(III) chelates was therefore assigned to a $\pi^* \rightarrow d$ transition.

Crosby and co-workers (23) in 1968 reconsidered the data and reassigned the emission of Ru(II)-imine complexes as charge transfer phosphorescence, ($^3\pi^* \rightarrow d$) in agreement with Paris's original work in 1959 (12). They prepared a series of <u>cis</u>-substituted <u>bis</u>-(2,2'-bipyridine)-ruthenium (II) chelates in which two adjacent coordination positions were occupied by mono- or bidentate ligands giving a wide range of ligand fields - <u>e.g</u>., cyanide, chloride, pyridine, ethylenediamine, and oxalate. The energy of the visible absorption band did not vary as would be predicted by the positions of these ligands in the spectrochemical series and therefore, this absorption band does not arise from a ligand field ($d^* \leftarrow d$) transition. In addition the energy of the emission band behaved in the same manner as the absorption, indicating that it too results from a charge transfer transition and is not $d^* \rightarrow d$.

Demas and Crosby (24) and Lytle and Hercules (25) measured the low temperature (77°K) luminescence lifetimes of the emitting states of some (charge transfer) luminescent ruthenium(II)-imine chelates as 0.5 - 10μ sec in rigid media. These are at least an order of magnitude shorter than the lifetimes usually measured for phosphorescence ($\geq$ msec) and an order of magnitude longer than for normal fluorescence ($\sim$ 10 nsec). Based partly upon these lifetime measurements, the charge transfer luminescence was assigned as a phosphorescence $[^3(\pi^*,d) \rightarrow {}^1A_1]$; the abnormally short lifetime of the triplet state was attributed to the heavy atom effect (ruthenium) which increases spin-orbit coupling and which causes an increased rate of intersystem crossing.

Recently (25) Lytle and Hercules published the complete assignment of the luminescence of tris-(2,2'-bipyridine)-ruthenium(II) dichloride. They measured the appropriate rate constants for phosphorescence, triplet internal conversion, singlet internal conversion, fluorescence, and intersystem crossing and assigned the emission as a charge transfer, spin forbidden T → S luminescence in which the heavy metal atom species increased spin-orbit coupling and enhanced the probability of S - T transitions to produce an abnormally short-lived phosphorescence.

Most complexes of transition metal ions are paramagnetic and thus do not fluoresce in fluid solution. This has seriously limited the development of analytical methods for the determination of transition metals based on measurements of luminescence intensity. However, several methods using the room temperature charge transfer luminescence have been developed. The luminescent chelate, tris-(5-methyl-1,10-phenanthroline)-ruthenium(II) was used in the determination of that metal (26). A procedure was developed by Fink and Ohnesorge (29) for the determination of iridium based on measuring the luminescence intensity of the Ir(III)-(2,2',2''-terpyridine) chelate. Ppm amounts were detected with an accuracy and precision of ca. 2% in the first case and 5% in the latter case.

In summary, $\pi^* \rightarrow m$ charge transfer luminescence may be expected for diamagnetic transition metal ion chelates when the charge transfer excited state is at lower energy than any (d^*,d) or (π^*,π) excited state, i.e., when the metallic ion is easily oxidized and the ligand accepts electrons readily (available π^* orbitals) and produces large ligand field splitting (large Dq).

3. $m^* \rightarrow \pi$ Fluorescence of Metal Complexes

Halide complexes of Tl(I), Sn(II), and Pb(II) fluoresce in solution (28). Results of recent studies of thallous halide complexes suggest that a charge transfer electronic transition from the halide ion to the metallic ion occurs on absorption and the reverse charge transfer transition is responsible for the fluorescence (29).

4. $m^* \rightarrow m$ Fluorescence of Metal Complexes

Complexes showing $m^* \rightarrow m$ emission give rise to emission spectra that are characterized by a relatively narrow, almost line-like, band. The transitions involve an electronic transition between (d or f) atomic orbitals of the metal ion. These transitions are LaPorte forbidden, $\Delta \ell = 0$ and may also be multiplicity forbidden; thus, the luminescence is usually very weak. This type of line-like emission has been reported and most intensively studied in certain rare-earth, Cr(III), and Cu(II) complexes (12,30-34).

The $f^* \rightarrow f$ transitions in rare earth complexes are only slightly affected by the presence of the ligand and the characteristic "line" positions can be predicted fairly accurately. Winefordner (35) has made use of this to analyze for various rare earths without prior separation. Similar luminescence from metal ion chelates in which the transition is between d orbitals ($d^* \rightarrow d$) is not as predictable because the d-orbitals of the metallic ion interact strongly with the ligand. The ligand field causes a splitting of the energy of the (outer) d-orbitals of the ion and the magnitude of the splitting is very dependent on the ligand. Also, the d-orbitals are capable of π-bonding with the ligand which again alters the energy between the various d states. Most experiments with $d^* \rightarrow d$ luminescence have been done using Cr(III) complexes in rigid glassy solutions due to the long lifetimes of the excited states; there are no analytical applications yet.

C. General Experimental

The general experimental procedures, specific methods, and techniques are developed within the experimental and results section of each topic.

D. Instrumentation

1. Absorption Spectra- Absorption spectra were recorded on either a Beckman Model DK-2A or on a Cary Model 14R recording spectrophotometer using 1.00-, 5.00-, and 10.00-cm. silica cells.

2. Luminescence Spectra - Luminescence measurements were made on a modified Farrand Model 104242 Spectrofluorometer. It was equipped with a General Electric UA-2 250-watt mercury lamp, an RCA 1P28 photomultiplier tube, and an RCA WV-84C microammeter. Emission spectra were recorded on a Hewlett-Packard Model 7035B X-Y recorder. The excitation monochromator was equipped with slits which gave effective

band widths of 20 nm. The emission monochromator slits gave widths of 10 nm for the entrance beam and 5 nm for the exit beam. The fluorescence cell was a 10 x 10 x 48 - mm quartz cell. All emission intensities are reported relative to the fluorescence intensity (450 nm) of a 1.0 ppm quinine sulfate in 0.1 _N_ - sulfuric acid solution excited at 366 nm and set to read 2.00 arbitrary emission units.

E. Low Temperature Luminescence Measurements

Absolute ethyl alcohol was used as the solvent for all low temperature observations. The ethanolic solutions were placed in the standard quartz cell and immersed in a liquid nitrogen bath until the rigid glass was formed, _ca_. 1 minute. For temperatures in the range -90°C to room temperature an ethanol slush bath was used to cool the samples. The temperature measurements were made with a toluene thermometer.

II. THORIUM(IV)-8-QUINOLINOL COMPLEXES RE-EXAMINATION OF THEIR COMPOSITION[36]

A. Introduction

The stoichiometry reported for the orange compound precipitated when aqueous solutions of thorium(IV) and 8-quinolinol (HQ) are mixed is $ThQ_4.HQ$ (37,38). Other cations have also been reported to form adducts with 8-quinolinol - e.g., $ZnQ_2.HQ$, $SrQ_2.2HQ$, $UO_2Q_2.HQ$ and $ScQ_3.HQ$ (39-42).

The extra 8-quinolinol molecule in the zinc compound occupies a coordination site on the metal ion (39). A structural analysis on the uranium adduct indicated a nearly planar arrangement of 8-quinolinol surrounding the uranium species, two as bidentates with bonds from both the phenolic oxygen and the ring nitrogen and one as a monodentate molecule bonded only from the phenolic oxygen (43,44). The acidic proton is titratable with strong base (41) and appears to be located on the ring nitrogen of the unidentate ligand; it is probably hydrogen-bonded to the phenolate oxygen of the neighboring bidentate ligand (43). Infrared studies appear to support this interpretation (45). This compound is perhaps best represented as $H[UO_2Q_3]$.

Recently it has been shown that the scandium compound obtained by precipitation is not an adduct as previously reported; rather it is the tris chelate compound, ScQ_3 (46).

An investigation of the chemical composition of the chelate formed between 2-methyl-8-quinolinol and thorium(IV) showed no evidence for the reported 5:1 adduct compound (47). In a later x-ray study the structure of a compound believed to be a 2-methyl-8-quinolinol adduct of thorium was shown to be identical with that of the *tetrakis* chelate compound (48).

Hecht and Reich-Rohrwig described an analytical procedure for the gravimetric determination of thorium using 8-quinolinol (49). The precipitated compound was reported as the monohydrate which when heated at 160° - 170°C rapidly converted to the anhydrous compound, ThQ_4. Bromination of the unheated sample, however, gave high results. This error could be avoided if the precipitate was previously washed with 25% alcohol. Frere also investigated the thorium precipitate by bromination and concluded that the material was an addition compound with the adduct composition, $ThQ_4.HQ$ (37). It was stable at 100° - 110°C, but slowly decreased in weight at 130° - 140°C. At 160° - 170°C conversion to the yellow 4:1 compound, ThQ_4, was complete; continued heating at this temperature resulted in further decomposition. Thermogravimetric investigations of the material have given varying ranges of heat stability (50-52).

Moeller and Ramaniah prepared an orange material, reported as the adduct compound, by precipitation from aqueous solution at pH 4.3 (38). The normal yellow 4:1 chelate was obtained by heating the orange material at 120° - 125°C for

5 hours and then at 130° - 135°C for 1 hour. The near-ultraviolet absorption spectra of nonaqueous solutions of the two substances differ only in absorption intensities. Beer's law was not followed, apparently due to hydrolytic decomposition of the chelate. However, drying the solvents with phosphorus pentoxide and with sodium hydride did not change the spectra.

It is generally believed that the adduct compound exists only in the solid state. The orange material dissociates completely to ThQ_4 and HQ in solution (38,53). In fact, merely washing the orange substance with methanol, with 95% ethanol, with chloroform, or with dichloroethane effects conversion to the yellow tetrakis chelate by selectively dissolving the extra 8-quinolinol molecules (49,53,45). Dissolving the orange material in dichloroethane that contains a large excess of 8-quinolinol results in the formation of a red solution (45). The red coloration has been attributed to the ion-pair $ThQ_5^-.H_2Q^+$ formed from the products of the acid-base reaction

$$ThQ_4.HQ + HQ \rightarrow ThQ_5^- + H_2Q^+$$

Further studies of the red coloration using ^{14}C-labeled 8-quinolinol in dichloroethane solution have shown the adduct is inert to 8-quinolinol exchange (54). In contrast, ThQ_4 under the same conditions exchanged rapidly until equilibrium was established in ca. 180 minutes. These results suggest all HQ molecules in the adduct compound are bidentate.

The infrared spectrum of the thorium adduct exhibits a broad band at ca. 2625 cm^{-1} and a very weak band at ca. 2100 cm^{-1} which are quite similar to those observed in the spectrum of the uranium adduct (55). For the deuteriated HQ adduct, the bands are shifted to about 2050 cm^{-1} ($\nu H/\nu D$ = 1.29) and 1510 cm^{-1} ($\nu H/\nu D$ = 1.37). These bands, which are also present in the spectra of the hydrochloride salts of HQ derivatives, are characteristic of the hydrogen-bonded $^{+}N-H...O$ system (45,55). On the basis of the (^{14}C)-experiments described in the previous paragraph and these infrared data it has been suggested that the HQ molecule in the adduct is coordinated as a zwitter-ion through the phenolate oxygen (45,54).

Unlike the scandium-8-quinolinol and the thorium-2-methyl-8-quinolinol systems there are clearly two different thorium 8-quinolinol materials: one yellow, the other orange. The assignment of the composition of the orange material as $ThQ_4.HQ$ appears to depend largely on the results of duplicate elemental analysis for carbon and hydrogen (28). Although there appears to be good agreement with the calculated values based on the $ThQ_4.HQ$ stoichiometry, it is important to realize that there was an error in the calculated carbon and hydrogen percentages for carbon and hydrogen in $ThQ_4.HQ$. The published values were 1% low for each of these elements.

Most observations on the orange material have been largely non-quantitative with regard to its composition - *i.e.*, the results require only that it contain excess 8-quinolinol, not necessarily in the exact 1:1 HQ:ThQ_4 mole ratio. There were, however, two instances reported where preparations gave compounds having HQ:ThQ_4 ratio of 4.8:1, (56,57). Corsini noted the composition of the adduct material was very sensitive to experimental conditions and the procedure he developed gave a material in which the average ratio of ligand-to-metal was 4.9:1. The adduct material was prepared by precipitation from an aqueous ammonium acetate solution by gradual addition of ammonium hydroxide (1.0 *M*) until the pH was 6-7. Moeller and Ramaniah (38) precipitated the orange material from solution on lowering the pH to 4.3 by the thermal decomposition of urea.

The present work is a re-investigation of the composition of thorium(IV)-8-quinolinol complexes. The results show that the material formed by precipitation from aqueous solution is a non-stoichiometric mixture which can best be represented by the formula $ThQ_4.xHQ$ where x is approximately 0.6. The deviations from Beer's law observed in absolute ethanol solution result from the partial dissociation of *tetrakis*-(8-quinolinolato)thorium(IV) to lower chelate species and 8-quinolinol.

B. Experimental Section

Reagents and Solutions. - The absolute ethyl alcohol (U.S. Industrial Chemicals Co.) used to prepare all stock and test solutions contained ca. 5 ppm water. Thorium nitrate tetrahydrate (J. T. Baker Chemical Co.) was used as obtained. The 8-quinolinol obtained from the Fisher Scientific Company was recrystallized from absolute methanol.

The method of Moeller and Ramaniah (38) was used to precipitate the orange 8-quinolinol-thorium(IV) chelate compound. Conversion of this product to the yellow 4:1 chelate by heating gave somewhat inconsistent results. Instead, this chelate was crystallized from chloroform by dissolving the orange substance. Both products were air dried at room temperature and stored in a vacuum desiccator over phosphorus pentoxide.

Thorium stock solutions were prepared in absolute ethanol using thorium nitrate tetrahydrate that had been dried at 110°C for several hours; the thorium content was determined by titration of the thorium ion with a standard solution of the disodium salt of ethylenediamine tetracetic acid. Solutions for formation studies were prepared by mixing reagents in the following order: metal, ligand, and base.

Procedures. - Solution pH measurements were made spectrophotometrically using indicators as previously described. Acid dissociation constants and relevant molar absorptivities for the indicators have been tabulated (58,59).

Interpretation of the Chelation Data. - The amounts of 8-quinolinol present in each of the several forms (free, HQ; conjugate acid, H_2Q^+; and chelated with thorium ion, Q') can be calculated as appropriate from measurements of the pH and the absorbance at 310 nm and at 365 nm. Appreciable amounts of the 8-quinolinolate ion, Q^-, were not involved in this study.

The absorption spectrum of 8-quinolinol (280 to 450 nm) consists of a single broad band (290 to 350 nm) with a peak near 315 nm. The molar absorptivities in absolute ethyl alcohol at 310 nm and at 365 nm are 2.6×10^3 and ca. 0.1×10^3, respectively. The pK_a for this species in absolute ethyl alcohol (determined spectrophotometrically with the indicators used in the present work) is 14.3 (60).

The most prominent band in the absorption spectrum of 8-quinolinium ion appears between 340 nm and 420 nm. Weaker peaks are present near 310 nm and near 320 nm. The molar absorptivities are 1.2×10^3 at 310 nm and 1.7×10^3 at 365 nm. The pK_a of this species in absolute ethyl alcohol is 6.3 (60).

The absorption spectra over the same wavelength region of 8-quinolinol chelates are quite similar to each other and to that of the 8-quinolinium ion provided ligand field and charge transfer bands are absent. The position of the bands

The extent of chelation is expressed as $\bar{n}_Q$, the average number of 8-quinolinol species bound to a thorium ion. The fluorescence data are used primarily to detect changes in the structure of the fluorescent species in the solution.

C. Results and Discussion

An analysis of the amount of thorium present in each of the thorium-8-quinolinol compounds was attempted by several methods; titration of the thorium with EDTA using a mercury-mercury(II) indicator electrode (61), titration with EDTA using the visual indicator xylenol orange (62), and by ignition of the compound to thorium dioxide. The results of the various analyses for thorium were erratic and no firm conclusion as to the composition of the materials could be made based on these data.

Table I shows the carbon, hydrogen, and nitrogen content of the orange and the yellow thorium(IV)-8-quinolinol compounds prepared as described above. There is good agreement with experimental results reported by earlier workers (38). These data indicate that the yellow compound is the 4:1 chelate, *tetrakis*(8-quinolinolato)-thorium(IV). However, because there was an error in the calculated values for the carbon and hydrogen content in an earlier work, the apparent agreement between the theoretical and the experimental analytical results for these elements on the orange compound was misleading (38). Thus, the adduct composition proposed,

ThQ_4.HQ, is not justified on the basis of these data and may not be correct. Further study of the composition of the orange material is in order.

The calculated carbon and hydrogen values, shown also in Table I for several non-stoichiometric combinations of ThQ_4 and HQ, suggest that the composition of the orange substance is most nearly approximated as ThQ_4.0.6 HQ. Additional data presented and discussed below provide further support for this tentative assignment and conclusion. This material is very hygroscopic; this property may have caused the high analytical result for hydrogen.

Tetrakis(8-quinolinolato)-Thorium(IV). - The near-ultraviolet absorption spectrum of solutions prepared by dissolving the yellow compound in absolute ethanol was typical of an 8-quinolinol chelate of a nontransition metal ion, Figure 3. The fluorescence excited by 365 nm radiation was (like that from many other 8-quinolinol chelates) yellow-green in color; (63) the emission spectrum was a single broad band (peak width at half-max-height *ca*. 50 nm) with a peak *ca*. 515 nm and did not vary with the chelate concentration: 0.003 to 0.16 *mM*.

Absorption data from these solutions are summarized in Table II; the pH was *ca*. 9.5, thus any non-chelated ligand was present in the molecular form, HQ. Solutions more dilute than *ca*. 0.14 *mM* show deviations from Beer's Law: positive

TABLE I

Carbon, Hydrogen, and Nitrogen Content of Thorium(IV)-8-Quinolinol Chelate Compounds

		Percent		
Compound		Carbon	Hydrogen	Nitrogen
ThQ_4	Calculated	53.47	2.99	6.93
ThQ_4.0.4 HQ	Calculated	54.87	3.12	7.11
ThQ_4.0.5 HQ	Calculated	55.20	3.15	7.15
ThQ_4.0.6 HQ	Calculated	55.51	3.17	7.19
ThQ_4.0.7 HQ	Calculated	55.81	3.20	7.23
ThQ_4.HQ	Calculated	56.67*	3.27*	7.34
Yellow	Found	53.57	3.08	6.90
Yellow	Found	53.49	3.08	7.08
Orange	Found	55.49	3.70	----
Orange	Found	55.59	3.78	----

---

*(3) - erroneously showed 55.6% carbon and 2.28% hydrogen for ThQ_4.HQ.

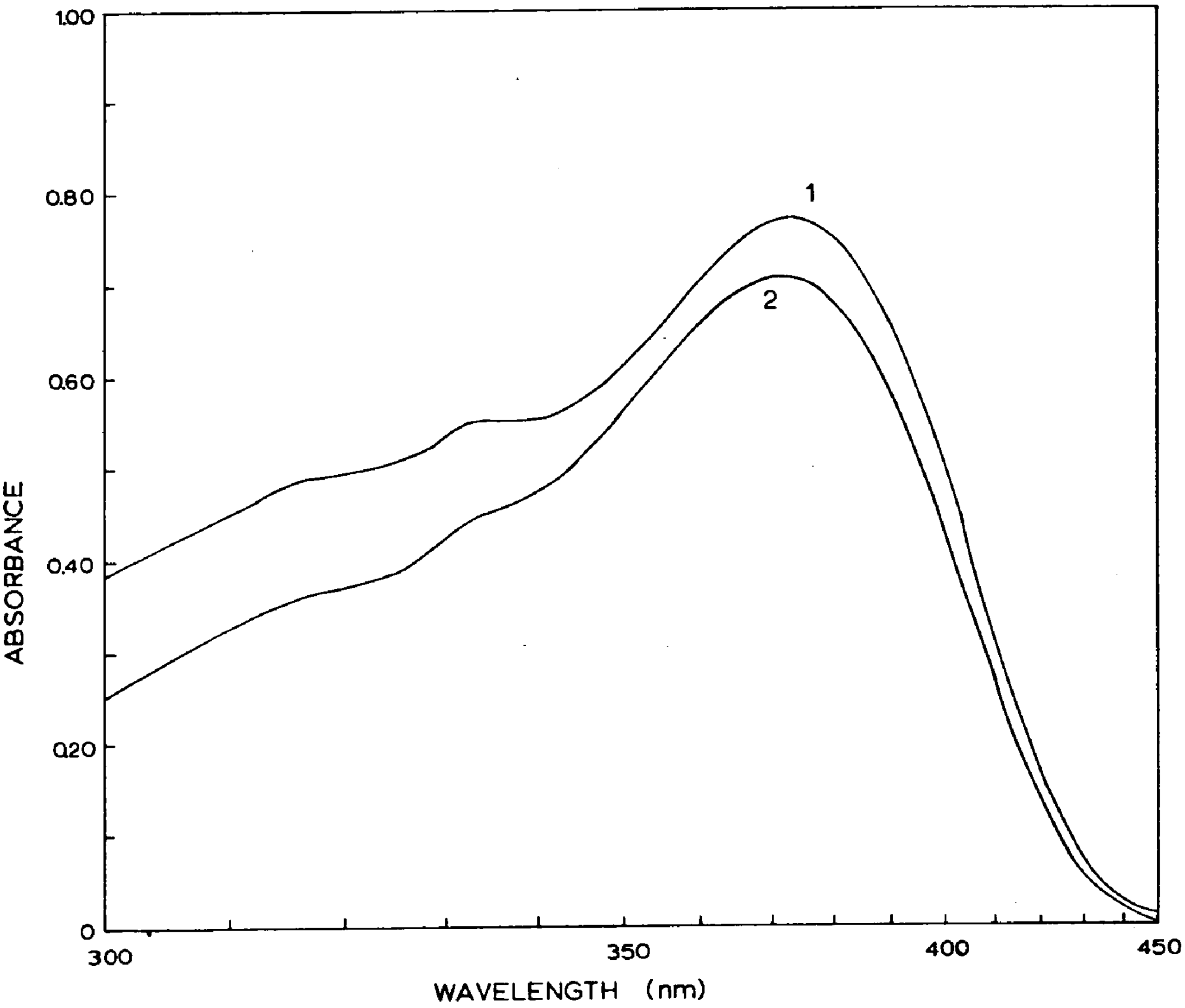
Figure 3

Absorption Spectra of Th(IV)-8-Quinolinol Complexes

Curve 1 - orange material; 0.0748 m$\underline{M}$ in $ThQ_4.06\ HQ$

Curve 2 - yellow compound; 0.0703 m$\underline{M}$ in ThQ_4

(1.00-cm. cells)



1.00
0.80
0.60
0.40
0.20
0
ABSORBANCE
300
350
400
450
WAVELENGTH (nm)
1
2

deviations at 365 nm, negative at 310 nm. The amounts of chelated and free ligand, calculated as previously described from absorbance data, are also given in Table II. The total ligand accounted for by these calculations agrees rather well with the amount known to be present as determined by the accurately measured quantity of *tetrakis*(8-quinolinolato) thorium(IV) used to prepare these solutions.

The extent of chelation, $\bar{n}_Q$, and the concentration of free ligand indicate that the 4:1 chelate dissociates to an appreciable extent in these dilute solutions to form free 8-quinolinol at the expense of the bound ligand. The equilibria appear to involve the *bis*-, *tris*-, and *tetrakis*-(8-quinolinol) chelate species:

$$ThQ_4 = ThQ_3 + HQ \qquad (1)$$

$$ThQ_3 = ThQ_2 + HQ \qquad (2)$$

The formal equilibrium constant for reaction (1) for the conditions of this experiment was estimated from the [$\bar{n}_Q$, HQ concentration] data for solutions more concentrated than 0.07 mM (64). At pH 9.5 K_1 is approximately 10^{-5}; because pK_a for HQ in absolute ethanol is 14.3, (60) a step-wise formation constant, K_4, of *ca*. 10^{10} for ThQ_4 is indicated.

Optical Characteristics of the Orange Material in Absolute Ethanol Solution. - Figure 3 shows the absorption spec-

TABLE II

Concentration Effects on Optical Properties of Tetrakis(8-Quinolinolato) Thorium(IV), ThQ_4, in Absolute Ethanol Solution

Th(IV) Conc. (mM)	Fluorescence* Intensity (515 nm)	$\varepsilon \times 10^{-3}$		8-Quinolinol			
				Found by Calculation			
		310 nm	365 nm	$\bar{n}_Q$	HQ (mM)	Total Q (mM)	Taken (mM)
0.1594	0.50	4.76	9.96	3.98	0	0.635	0.638
0.1434	0.50	4.66	9.90	3.96	0	0.568	0.574
0.1275	0.50	4.77	9.80	3.91	0.004	0.503	0.510
0.1116	0.51	4.91	9.75	3.91	0.010	0.444	0.446
0.09563	0.51	4.86	9.54	3.81	0.011	0.375	0.383
0.07969	0.50	5.01	9.40	3.75	0.015	0.314	0.319
0.06375	0.47	5.11	9.15	3.65	0.018	0.251	0.255
0.04781	0.42	5.02	8.89	3.53	0.017	0.186	0.190
0.03825	0.38	5.39	8.81	3.50	0.017	0.151	0.153
0.03188	0.34	5.46	8.58	3.42	0.017	0.126	0.128
0.02550	0.29	5.49	8.41	3.34	0.015	0.100	0.102
0.1913	0.24	5.71	8.29	3.29	0.0130	0.0759	0.0765
0.01275	0.18	6.15	7.83	3.09	0.0120	0.0514	0.0510
0.00953	0.15	5.73	7.91	3.14	0.0072	0.0371	0.0381
0.00858	0.13	5.82	7.95	3.15	0.0067	0.0337	0.0343
0.00763	0.12	5.99	7.82	3.09	0.0067	0.0303	0.0305
0.00667	0.10	6.30	7.63	3.01	0.0062	0.0263	0.0267
0.00572	0.088	6.10	7.24	2.85	0.0059	0.0222	0.0229
0.00477	0.074	6.35	6.56	2.58	0.0060	0.0183	0.0191
0.00381	0.061	6.51	6.51	2.55	0.0050	0.0148	0.0152
0.00286	0.045	6.68	5.87	2.26	0.0043	0.0109	0.0114

*Given in arbitrary units based on 1.0 ppm quinine sulphate in 0.10 N H_2SO_4 excited by 365 nm radiation showing fluorescence intensity of 2.0 arbitrary scale units at 450 nm.

trum of an absolute ethanol solution of the orange material and, for comparison, a spectrum of a similar solution of the yellow compound. For comparable thorium concentrations the principal difference is the broad band near 310 nm; its intensity is much greater in the spectrum of the orange compound.

Solutions prepared by dissolving the orange substance in absolute ethanol do not obey Beer's Law. Typical results in Table III show the deviation is positive at 365 nm and negative at 310 nm. The amounts of free and chelated 8-quinolinol present in these solutions were calculated from the absorbance data as before. There was again good agreement between the total amounts of 8-quinolinol calculated and taken, based on the composition $ThQ_4.0.6\ HQ$ as determined by the carbon-hydrogen analytical results. The formal equilibrium constant for reaction (1) based on these data and experimental conditions was calculated as before; K_4 agreed very well with the results of the previous calculation - ca. 10^{10}. Fluorescence data obtained on these solutions showed a broad emission band with maximum emission at 515 nm; it did not shift with concentration changes 0.005 to 0.12 mM.

Comparison of Spectra. - Figure 4 shows absorption spectra of absolute ethanol solutions prepared (1) by dissolving the orange substance and (2) by mixing thorium ion, 8-quinolinol, and base. The thorium concentration of the two solutions is approximately the same and the ligand-to-metal ion

TABLE III

Concentration Effects on Optical Properties of the Orange Compound in Absolute Ethanol

				8-Quinolinol			
				Found by Calculation			
Th(IV) Conc. (mM)[a]	Fluorescence[b] Intensity (515 nm)	$\epsilon \times 10^{-3}$					
		310 nm	365 nm	$\bar{n}_Q$	HQ (mM)	Total Q (mM)	Taken (mM)
0.1208	0.50	6.42	9.94	3.95	0.078	0.555	0.558
0.1087	0.50	6.38	9.81	3.90	0.067	0.491	0.502
0.09666	0.50	6.34	9.70	3.86	0.063	0.436	0.446
0.08457	0.50	6.43	9.67	3.84	0.059	0.384	0.390
0.06041	0.46	6.62	9.58	3.81	0.048	0.278	0.279
0.04832	0.42	6.83	9.42	3.73	0.043	0.223	0.223
0.04349	0.39	6.90	9.33	3.70	0.041	0.202	0.201
0.03866	0.36	6.85	9.29	3.67	0.037	0.179	0.178
0.03382	0.34	7.10	9.11	3.61	0.036	0.158	0.156
0.02899	0.30	7.17	8.97	3.55	0.032	0.135	0.134
0.02416	0.26	6.70	8.44	3.34	0.0250	0.1056	0.111
0.01933	0.21	6.79	8.00	3.15	0.0223	0.0832	0.0892
0.01449	0.17	7.11	7.48	2.94	0.0200	0.0626	0.0669
0.009665	0.12	7.39	6.06	2.36	0.0169	0.0397	0.0446
0.004832	0.055	7.86	3.72	1.39	0.0115	0.0182	0.0223

[a] Based on carbon-hydrogen analysis, the formula is $ThQ_4 \cdot 0.6\ HQ$ and the calculated thorium content 25.84%.

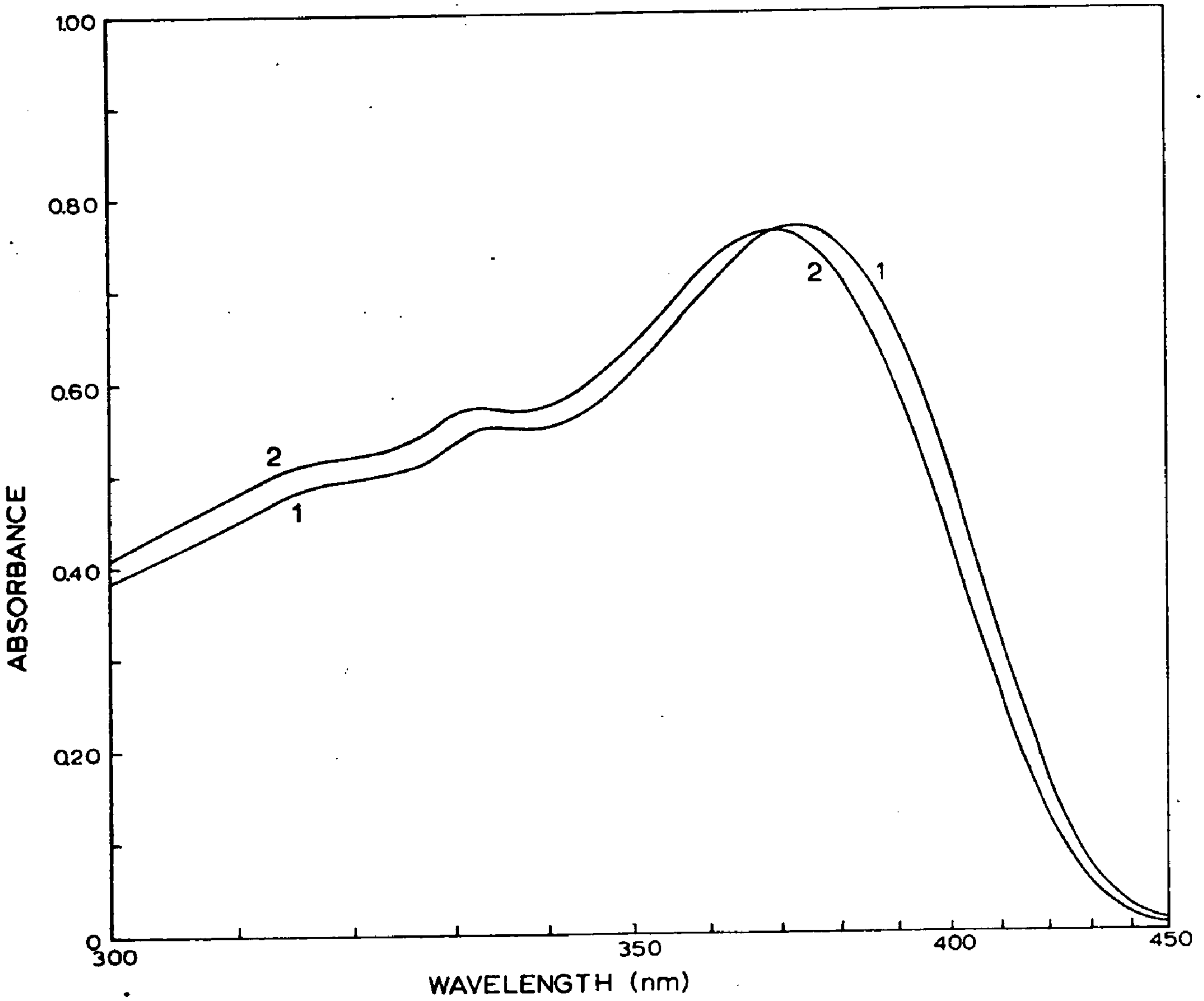
[b] Given in arbitrary units based on 1.0 ppm quinine sulphate in 0.10 N H_2SO_4 excited by 365 nm radiation showing fluorescence intensity of 2.0 arbitrary scale units at 450 nm.

Figure 4

Absorption Spectra of Th(IV)-8-Quinolinol Complexes

Curve 1 - orange material; 0.0748 m*M* in $ThQ_4 \cdot 0.6\ HQ$

Curve 2 - 0.0752 m*M* in Th(IV),
0.353 m*M* in HQ, and
0.376 m*M* in NaOH
(1.00-cm. cells)


1.00
0.80
0.60
0.40
0.20
0
ABSORBANCE
300
350
400
450
WAVELENGTH (nm)
1
2
2
1

mole ratio in the second solution is 4.7. The spectra are quite similar; the most significant difference is the somewhat higher absorbance of the solution (2) prepared by mixing the metal ion and the ligand in the region of the free 8-quinolinol absorption, 310 nm.

Table IV shows the results of calculations of free and bound ligand concentrations for both solutions; $\bar{n}_Q$ and total amounts of 8-quinolinol calculated are in very good agreement with each other; the latter agree also with the values expected based on the known amounts of material used to prepare these solutions.

Table IV also compares the absorbances at 310 nm and at 365 nm and the calculated amounts of free and chelated ligand calculated for two additional solutions. One of these solutions (3) was prepared by mixing thorium ions and 4.6 times the molar quantity of 8-quinolinol plus base; the other solution (4) contained the yellow chelate compound, ThQ_4, plus 0.6 times as many moles of 8-quinolinol. The absorption spectra were nearly identical, as expected from the almost equal amounts of thorium(IV) present and of ligand added in preparing the solutions.

These results are clear indication that all the above four solutions contain an excess of 8-quinolinol. More important, the solution prepared with ligand-to-thorium mole ratio of 4.6 (3) contains a slightly smaller quantity and

TABLE IV

Concentration Data for Solutions (1) - (4)

					8-Quinolinol			
					Found by Calculation			
	Solution Number and Composition	Th(IV) Conc. (m$\underline{M}$)	Absorbance[a] 310 nm	Absorbance[a] 365 nm	$\bar{n}_Q$	HQ Conc. (m$\underline{M}$)	Total Q (m$\underline{M}$)	Taken (m$\underline{M}$)
(1)	(orange material)	0.0748	0.453	0.742	3.94	0.049	0.344	0.346
(2)	Th(IV) + 4.7 HQ + base	0.0752	0.478	0.753	3.96	0.058	0.356	0.353
(3)	Th(IV) + 4.6 HQ + base	0.0752	0.453	0.751	3.95	0.048	0.345	0.346
(4)	ThQ_4 + 0.6 HQ	0.0749	0.470	0.737	3.91	0.045	0.338	0.345

[a] 1.00 cm cells

that with the 4.7 mole ratio (2) contains a slightly larger quantity of free 8-quinolinol than the solution (1) prepared from the orange material.

These results confirm the earlier assignment of the orange material as a non-stoichiometric mixture of <u>tetrakis</u> (8-quinolinolato)thorium(IV) and 8-quinolinol with a ligand: chelate ratio of <u>ca</u>. 0.6 rather than 1.0 as previously believed. These data also suggest that an earlier conclusion that there is no association between the 4:1 chelate species and the excess 8-quinolinol in solution is probably correct.

Mole Ratio Study. - To seek other evidence for association between ThQ_4 and the excess HQ in solution and to obtain additional confirmation of the above conclusions, a mole ratio study of the complexation of thorium(IV) with 8-quinolinol in absolute ethanol solution was performed. Figure 5 shows the results obtained on solutions containing the same amounts of thorium ion and base with a [base/metal ion] mole ratio of 5. The pH of each of these solutions was between 9.5 and 10.5, thus any uncomplexed ligand would exist in the molecular form, HQ.

Breaks in the absorbance curves at a ligand-to-metal mole ratio of <u>ca</u>. 4 confirm the formation of a chelate with four ligands bound to each thorium ion. Furthermore these data provide no evidence for the formation of additional complexes: the absorbance of 365 nm does not increase and there is the

Figure 5

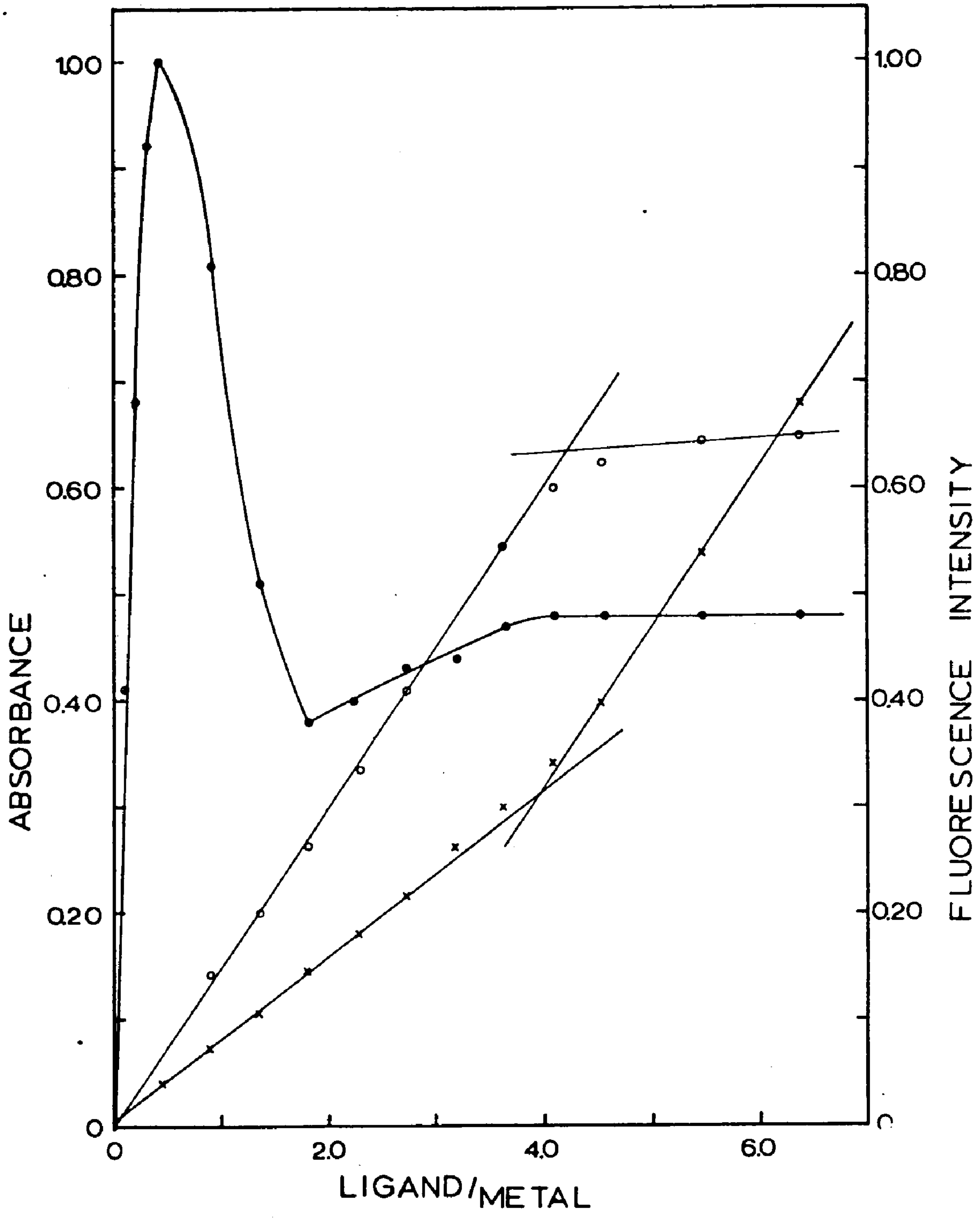
Mole Ratio Study

0.0627 m$\underline{M}$ Th(IV)

. - Fluorescence Intensity at 515 nm (365 nm excitation).

o - Absorbance at 365 nm (1.00 - cm cells).

x - Absorbance at 310 nm (1.00 - cm cells).



ABSORBANCE
FLUORESCENCE INTENSITY
LIGAND/METAL
0
0.20
0.40
0.60
0.80
1.00
2.0
4.0
6.0

expected increase in the slope of the 310 nm absorbance curve (the molar absorptivity at 310 nm for 8-quinolinol is ca. twice that for the chelated ligand) when the ligand to metal mole ratio exceeded four. Moreover, amounts of 8-quinolinol calculated from these absorbance data show not only an upper limit of 4 for $\bar{n}_Q$, but the total amount of 8-quinolinol found also agrees rather well with the known amount taken, Table V.

The wavelength of maximum luminescence emission from these solutions increased from ca. 488 nm (when the ligand-to-metal mole ratio was about 0.05) to approximately 515 nm when the ratio exceeded 3. Thus there is a change in the identity of the major fluorophore as the ligand-to-metal ion mole ratio is increased. Maximum fluorescence intensity was recorded when the ligand-to-metal ion mole ratio was ca. 0.4 which suggests that a lower thorium-8-quinolinol complex, ThQ or perhaps ThQ_2, is more intensely fluorescent than the 3:1 and 4:1 chelate species. Red shifts in the wavelength of maximum fluorescence with increasing ligand concentration as well as very high luminescence emission intensity from lower chelate species have been reported for 8-quinolinol chelates of some other metal ions - Sc, In, and Al (46,58,60) and for aluminum ion-flavanol complexes (65). The formal equilibrium constant for Reaction (1) was calculated from these [$\bar{n}_Q$ and 8-quinolinol concentration] data. The K' at pH 10 is approximately 10^{-6} and corresponds to a stepwise formation constant, K_4, of 10^{10} for tetrakis-(8-quinolinolato)thorium(IV).

TABLE V

. Mole Ratio Study of Th(IV)-8-Quinolinol Complexation

HQ Added mM	$\left[\frac{HQ}{Th}\right]$	Absorbance		Fluorescence[a]		Found by Calculation		
		310 nm	365 nm	Intensity 515 nm	λ max nm	$\bar{n}_Q$	HQ Conc. (mM)	Total Q
0.002841	0.045	------	------	0.26	488	----	-------	-------
0.005683	0.091	------	------	0.41	490	----	-------	-------
0.08525	0.136	------	------	0.53	492	----	-------	-------
0.01138	0.181	0.140[b]	0.250	0.63	495	0.16	0.00077	0.0107
0.01421	0.227	0.173	0.325	0.71	495	0.21	0.00065	0.0137
0.01705	0.272	0.210	0.401	0.78	495	0.26	0.00069	0.0167
0.01989	0.317	0.244	0.244	0.90	495	0.31	0.00058	0.0197
0.02275	0.363	0.277	0.553	0.92	495	0.35	0.00046	0.0226
0.02558	0.408	0.298	0.622	1.0	495	0.40	0	0.0249
0.02842	0.453	0.333	0.695	1.0	495	0.44	0	0.0278
0.05683	0.91	0.360[c]	0.703	0.81	495	0.90	0.0018	0.0580
0.08525	1.36	0.528	0.998	0.51	502	1.27	0.0038	0.0835
0.1138	1.81	0.288[d]	0.526	0.38	505	1.67	0.0069	0.112
0.1421	2.27	0.357	0.670	0.40	508	2.14	0.0068	0.141
0.1705	2.72	0.423	0.816	0.43	511	2.60	0.0080	0.171
0.1989	3.17	0.263[e]	0.435	0.44	515	2.76	0.021	0.194
0.2275	3.63	0.299	0.545	0.47	515	3.46	0.015	0.232
0.2558	4.08	0.340	0.600	0.48	515	3.81	0.020	0.259
0.2842	4.53	0.397	0.624	0.48	515	3.96	0.030	0.278
0.3418	5.45	0.540	0.645	0.48	515	4.05	0.090	0.344
0.3987	6.36	0.680	0.649	0.48	515	4.05	0.144	0.398
0.4557	7.27	0.828	0.649	0.48	515	4.00	0.203	0.454

All solutions: 0.0627mM in Th(IV) and 0.3mM in added base; pH approximately 10.

[a] Given in arbitrary units based on 1.0 ppm quinine sulphate in 0.10 N H_2SO_4 excited by 365 nm radiation showing fluorescence intensity of 2.0 arbitrary scale units at 450 nm., [b] 10.0-cm cells, [c] 5.00-cm cells, [d] 2.00-cm cells, [e] 1.00-cm cells

III. EFFECT OF LIGAND FIELD STRENGTH ON CHARGE TRANSFER LUMINESCENCE OF SEVERAL BIS-(1,10-PHENANTHROLINE)-RUTHENIUM(II) CHELATES

A. Introduction

Transition metal ion chelates are usually not luminescent in fluid solution because most of these species are paramagnetic due to the partly-filled outer-shell d orbitals. Paramagnetic species undergo intersystem crossing rapidly which usually quenches luminescence efficiently. Thus, only diamagnetic complexes may be expected to luminesce (3).

Several Ru(II)-imine chelates (d^6, octahedral microsymmetry, low-spin) show an intense red-orange luminescence at room temperature (12). Recent work (24,25) has confirmed that the emission accompanies a ligand-to-metal charge-transfer transition ($\pi^* \rightarrow d$) in which the excited state is a ligand triplet ($^3\pi^*$); thus, it is a phosphorescence. Some imine chelates of Ir(III) and Os(II) also show a charge-transfer luminescence (19,66); in some cases this radiation is also emitted by samples in fluid solution at room temperature (27).

It is interesting to note, however, that not all diamagnetic transition metal ion chelates having low energy charge transfer excited states emit charge transfer luminescence. There is complete absence of luminescence from Fe(II)-imine chelates between room temperature and at least ca. 80 K.

Also, 2-methyl-1,10-phenanthroline-Ir(III), tris-(2-methyl-1,10-phenanthroline-Ru(II), and bis-(2,2',2"-terpyridine)-Ru(II) are non-luminescent at room temperature; however, luminescence is observed from these species when examined in absolute ethanol glasses at *ca*. 80°K (67). Moreover, the intensity of $\pi^* \rightarrow d$ charge transfer luminescence is very strongly temperature dependent (24,27), considerably more so than $\pi^* \rightarrow \pi$ luminescence.

Fink and Ohnesorge have attributed the large temperature effect on the luminescence intensity of some Ir(III)- and Ru(II)-imine chelates to the effect on the intersystem crossing rate and on the energy of excited ligand field states of a temperature-dependent equilibrium between high- and low-spin configurations (π^*, $e_g^2 t_{2g}^3 \rightleftarrows \pi^*$, t_{2g}^5) established during the lifetime of the charge-transfer excited state (π^*,d) of the chelate (67). The luminescence intensity of the chelate will be decreased approximately in proportion to the extent of cross-over to the high-spin paramagnetic excited state.

Investigations of the spin properties of some Fe(II)-imine chelates show all of the lower complexes are high spin and paramagnetic, but the highest complexes (tris imine species of 2,2'-bipyridine, 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, and the bis species of 2,2',2"-terpyridine) are diamagnetic (68). These spin-state changes are reflected by an abnormally large stepwise formation constant for those chelates whose formation accompanies the conversion from a high- to a low-spin species.

Considerable interest has recently been directed to studying the temperature dependence of the magnetic properties and the identification of spin-crossover points for complexes that are capable of existing both in high-spin and low-spin configurations (69-73). Studies of the temperature dependence of the magnetic properties of the tris-(2 methyl-1,10-phenanthroline)-Fe(II) complex ion by Goodwin and Sylva indicate the complex is a high-spin species at room temperature (74). Steric hindrance due to the methyl group on the 2 position of the phenanthroline prevents the ligand from approaching the ferrous ion sufficiently closely to provide a ligand field strength of adequate magnitude to form a low spin complex. Upon cooling, the magnetic moment of the complex becomes smaller, approaching 3 BM at 100°K, and behaves as expected if an equilibrium between approximately equienergetic high-spin (t_{2g}^4,e_g^2) and low-spin (t_{2g}^6) configurations were shifting to favor increased population of the low-spin state as the temperature is lowered: $^1A_1 \rightleftarrows {}^5T_2$. Accompanying the change in spin states will be a decrease metal ion-ligand bond distance and an increase in the ligand field strength (74). An additional observation consistent with these explanations reported by Goodwin and Sylva is a change in the color of solutions containing the tris-(2-methyl-1,10-phenanthroline)-Fe(II) ion upon cooling; they attribute this to the enhancement of the metal-to-ligand charge-transfer absorption transition probability with decreased ligand-to-metal ion bond distance in the low-spin complex.

Steric effects were observed to be important in determining the excited state ligand field strength, Dq^*; thus, Fink and Ohnesorge found the imine chelates of Fe(II), the metal ion which would show the smallest ligand field splittings among those studied: Fe(II), Ru(II), Ir(III), show no luminescence even at the lowest temperatures. Sterically hindered ligands such as 2-methyl-1,10-phenanthroline, where the methyl group on the 2 position of the phenanthroline prevents the ligand from approaching the ruthenium-(II) ion closely, and terpyridine, whose structural rigidity likewise prevents a close approach, form chelates with ruthenium(II) that do not luminesce at room temperature but do emit the characteristic red-orange luminescence at the temperature of liquid nitrogen. With Ir(III), the metal ion that would be subject to the largest ligand field splittings, only the most hindered ligand, 2-methyl-1.10-phenanthroline, forms a chelate that fails to show charge-transfer luminescence in fluid solution although this chelate too emits in rigid media.

To gain additional support for this explanation and to emphasize further the importance of the phenomenon of excited state spin crossover on the emission properties of chelates showing $\pi^* \rightarrow d$ charge transfer luminescence a series of cis-substituted bis-(1,10-phenanthroline)-Ru(II) complexes, Ru (II)$(phen)_2X_2$, was prepared and studied. The ligand field due to the monodentate species X was varied over a wide range.

A similar series of *bis*-(bipyridine)-Ru(II) complexes was investigated by Klassen and Crosby in rigid media (23). They showed the *wavelength* of the emission from these *bis*-(bipyridine)-Ru(II) complexes did *not* depend on the identity of the *cis*-substitutent, X, indicating that the energy of luminescence is independent of the ligand field strength (Dq) produced by X. Largely on the basis of this evidence they assigned the red-orange Ru(II)-imine luminescence to a charge-transfer radiative transition. In this investigation the effect of the ligand field strength of X on the *intensity* of the charge transfer luminescence of several *bis*-(1,10-phenanthroline)-Ru(II) complexes as a function of temperature has been examined.

B. Experimental

All solutions were prepared using absolute ethyl alcohol (U.S. Industrial Chemicals Co.). Ruthenium trichloride hydrate (Alfa Inorganics, Inc.) was used to prepare potassium pentachloromonoaquoruthenium(III) (16), $K_2[Ru(III)Cl_5(OH_2)]$, which served as the starting material in the preparation of the *cis*-substituted *bis*-(1,10-phenanthroline)-Ru(II) complexes. 1,10-Phenanthroline monohydrate (G. Frederick Smith Chemical Co.) was used without further purification.

Potassium pentachloromonoaquoruthenate(III) (16) was prepared by dissolving ruthenium(III) chloride in 12 M hydrochloric acid and boiling for several hours. A stoichiometric amount of potassium chloride was added, and the solution was stirred with mercury until the solution became green, indicating the formation of some ruthenium(II). Mercurous chloride was removed by filtration, and the solution was evaporated to a small volume and cooled. The resulting red crystals were separated by filtering, washed with ethanol, and recrystallized from 6 M hydrochloric acid.

Phenanthrolinium Tetrachlorophenanthroline-ruthenium(III) 1-hydrate (75). - Phenanthroline monohydrate (7.2g) was added to potassium pentachloromonoaquoruthenate (III) (5.6 g), dissolved in HCl (1.0 N; 36.9 ml) at 30°C in a stoppered flask. The mixture was shaken vigorously to dissolve the base rapidly; crystallization was induced within 3 minutes by scratching the sides of the flask with a glass rod, and the mixture allowed to stand for 7-10 days at 30°C to complete the reaction. The light brown needles were collected, washed with cold water, and air-dried.

cis-Dichloro*bis*-1,10-phenanthrolineruthenium(II) (76). - Phenanthrolinium tetrachlorophenanthroline-ruthenium(III) 1-hydrate (1 g) was suspended in dimethylformamide (20 ml) and the mixture refluxed for 3 hours. The initially formed brown solution soon turned to a deep brown-violet and finally to a deep violet color. On cooling the product separated and was recrystallized from ethanol.

cis-Dicyano-_bis_-(1,10-phenanthroline)-ruthenium(II). - $Ru(II)(phen)_2(CN)_2$ was prepared by adding sodium cyanide (1.0 g) to a solution of $Ru(II)(phen)_2(Cl)_2$ (0.5 g) in methanol (10 ml) and water (10 ml); the solution was refluxed for 2 hours. Bright red crystals of the product formed on reducing the solution volume to _ca_. 10 ml.

All other complexes were prepared by procedures given in the literature references in Table VI. In general these involved heating solutions of $Ru(II)(phen)_2(Cl)_2$ and an excess of the auxiliary ligand species several hours under reflux. Neutral complexes crystallized from the reaction solution upon cooling while other species were precipitated from solution as perchlorate salts by addition of sodium perchlorate.

C. Results and Discussion

Absorption Spectra - All of these chelates show similar intense broad absorption bands near 500 nm, Figures 7-13. These bands arise from metal-to-ligand charge transfer transitions ($\pi^* \leftarrow d$) analogous to those observed with the _tris_-imine-Ru(II) chelates.

Mercer and Buckley (16) located the lowest-energy $d^* \leftarrow d$ transitions in $Ru(H_2O)_6^{+2}$ at _ca_. 18.9 kK (530 nm). Because each coordinated N atom will increase D_q by _ca_. 6% (22) (compared to H_2O), these ($d^* \leftarrow d$) excited states would be above

TABLE VI

Temperature Effects on the Luminescence of Ru(II)(phen)$_2$X$_2$ Chelates

Complex	Prep.	Conc. (mM)	Relative Intensity[a] 24°C	-196°C	$\lambda_{max}(\pi^* \leftarrow d)$
Ru(II)(phen)$_2$(Cl)$_2$	76	0.056	0	0	505 nm (pk) 460 nm (sh)
Ru(II)(phen)$_2$(C$_2$O$_4$).3H$_2$O	77	0.076	0	0	520 nm (pk) 470 nm (sh)
[Ru(II)(phen)$_2$(OH$_2$)$_2$][ClO$_4$]$_2$	78	0.055	0	0	490 nm (pk) 450 nm (sh)
[Ru(II)(phen)$_2$(pyr)(OH$_2$)][ClO$_4$]$_2$.2H$_2$O	77	0.049	0	0.71	450 nm (pk)
[Ru(II)(phen)$_2$(pyr)$_2$][ClO$_4$]$_2$.2H$_2$O	77	0.054	0.011	6.1	455 nm (pk) 415 nm (pk)
[Ru(II)(phen)$_2$(NH$_3$)$_2$][I]$_2$.2H$_2$O	77	0.206	0.0058	0.14	485 nm (pk) 460 nm (sh)
Ru(II)(phen)$_2$(CN)$_2$.4H$_2$O		0.043	0.12	0.90	460 nm (pk) 420 nm (sh)

[a] Given in arbitrary units based on 1.0 ppm quinine sulfate in 0.10 M H$_2$SO$_4$ excited by 365 nm radiation showing fluorescence intensity of 2.0 arbitrary scale units at 450 nm.

ca. 415 nm in the Ru(II)(phen)$_2$X$_2$ species investigated. This energy is less than that of the lowest phenanthroline (π^*,π) excited states and considerably above that of the (π^*,d) charge transfer excited states of these chelates. The charge transfer bands of the Ru(II)-imine chelates are also much more intense (ϵ ca. 10^3) than the ligand field $d^* \leftarrow d$ transitions. In several cases the components of the charge transfer bands are sufficiently separated that they may be discerned, Figures 11, 12.

Luminescence - Deaerated* absolute ethanol solutions of the chelates shown in Table VI were examined from ca. 50°C to 196°C (temperature of liquid nitrogen). Excitation of the chelates by the 436 nm or the 365 nm line from a low-pressure mercury arc yielded identical emission spectra; however, the 436 nm line was used exclusively because it populated the excited state more efficiently, thus producing more intense emission. The emission of the chelates consisted of a broad band with a peak at ca. 590 nm (except the bis-cyano-bis-phenanthroline-ruthenium(II) which emits at slightly lower energy, λ_{max} ca. 605 nm). No shift with temperature in the wavelength of maximum intensity was observed for the chelates that phosphoresce in the range room temperature to the temperature of liquid nitrogen.

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*A stream of nitrogen gas was passed through the sample solutions for ca. 5 minutes prior to making the luminescence measurements.

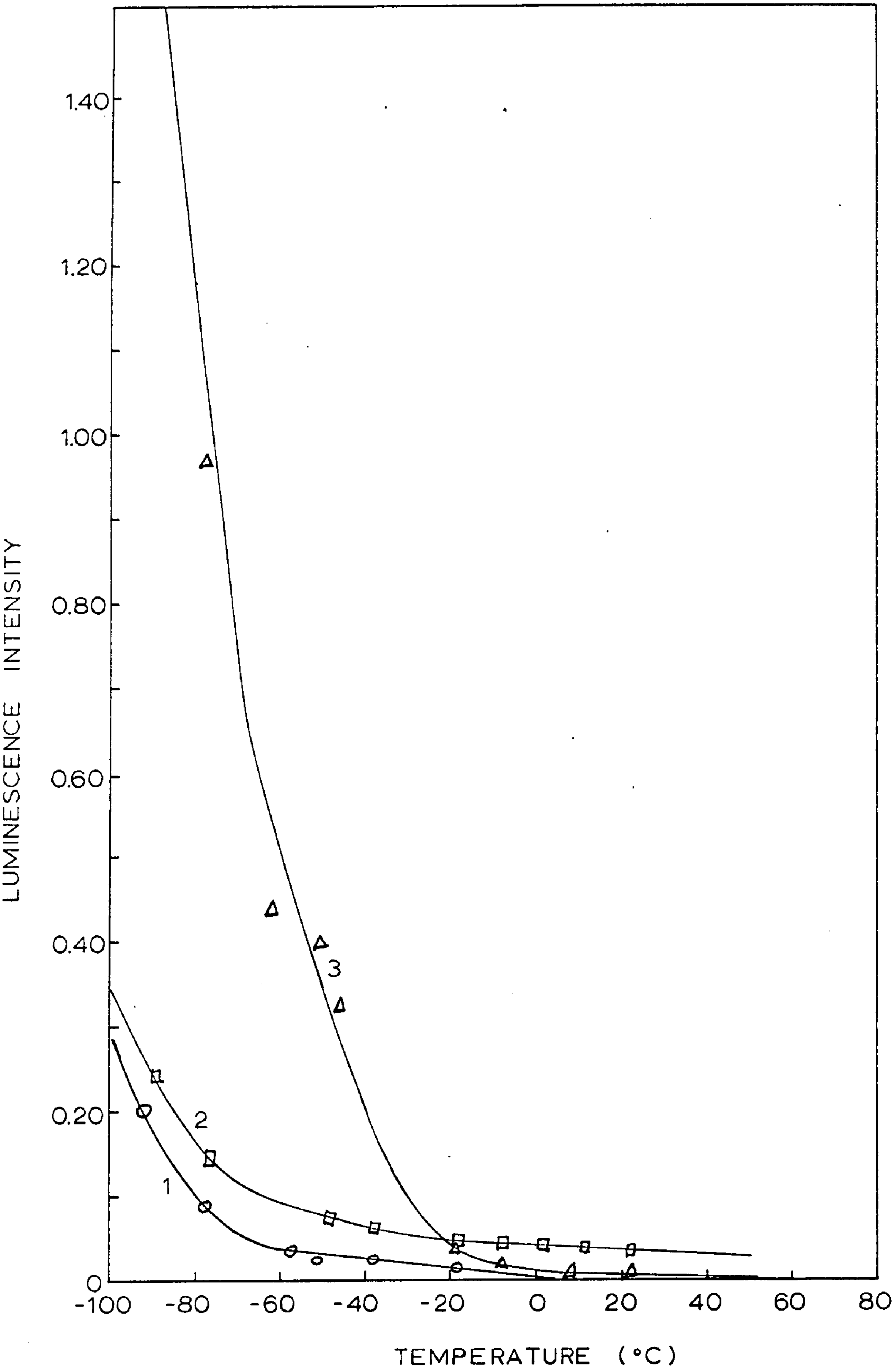
<u>Discussion</u> - The chelates are listed in Table VI in order of increasing ligand field strength of X on going down the Table -- <u>i.e.</u>, D_q of $Cl^- < C_2O_4^{2-} < H_2O <$ pyr $<< CN^-$. Although all these chelates are diamagnetic in the ground state, solutions of the first three imine species, which contain auxiliary ligands that produce weak ligand fields, show no luminescence -- even at liquid nitrogen temperature. The chelates <u>bis</u>-pyridine- and <u>bis</u>-cyano-<u>bis</u>-phenanthroline-Ru(II), $[Ru(II)(phen)_2(pyr)_2]^{2+}$ and $Ru(II)(phen)_2(CN)_2$, contain auxiliary ligands which produce a strong ligand field. This increase in the ligand field strength of X results in chelates which luminesce even in fluid solution at room temperature, Table VI. When the ligand field is increased slightly over the weak field cases by going to <u>mono</u>-aquo-<u>mono</u>-pyridine-<u>bis</u>-phenanthroline Ru(II), $[Ru(II)(phen)_2(pyr)(H_2O)]^{2+}$, the characteristic red-orange charge transfer luminescence is absent at room temperature, but the compound phosphoresces when the temperature is lowered to <u>ca</u>. 0°C; the luminescence intensity increases with further lowering of the sample solution temperature and is quite intense in glassy solutions at liquid nitrogen temperature. Figure 6 illustrates the marked temperature dependence of the luminescence intensity of some of these chelates.

The luminescence (or lack thereof) from these chelates appears related directly to the strength of the ligand field provided by the auxiliary ligand, X. There is also the pro-

Figure 6

Temperature Effects on Luminescence
Intensity of Ru(II)(phen)$_2$X$_2$ Species

1. [Ru(II)(phen)$_2$(pyr)(H$_2$O)][ClO$_4$]$_2$, 0.049 m<u>M</u>
2. Ru(II)(phen)$_2$(CN)$_2$, 0.043 m<u>M</u>
3. [Ru(II)(phen)$_2$(pyr)$_2$][ClO$_4$]$_2$, 0.054 m<u>M</u>


LUMINESCENCE INTENSITY
TEMPERATURE (°C)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0
-100
-80
-60
-40
-20
0
20
40
60
80
1
2
3

nounced increase in luminescence intensity with lowering the sample temperature. These observations are consistent with the existence of and tend to underscore the importance of the role played by the equilibrium between the low- and high-spin charge transfer excited state configurations (π^*, t_{2g}^5) and $(\pi^*, e_g^2 t_{2g}^3)$.

In the first three compounds listed in Table VI the ligand field splitting is apparently insufficient to provide stabilization for the low-spin excited state configuration (π^*, t_{2g}^5) and the high-spin configuration $(\pi^*, e_g^2 t_{2g}^3)$ is assumed by the excited species at all temperatures investigated. Thus, no luminescence is observed even at liquid nitrogen temperature. In the complexes containing cyanide and pyridine these ligands produce a sufficiently strong ligand field to stabilize, and thus favor high populations of, the lower energy low-spin (π^*, t_{2g}^5) configuration, particularly at low temperatures. Luminescence is therefore observed at room temperature as well as at 77°K. _Mono_-aquo-_mono_-pyridine-_bis_-phenanthroline-Ru(II) has a ligand field splitting that is intermediate in this series of complexes; this complex does not show luminescence until the temperature is lowered sufficiently (to _ca_. 0°C) such that position of the excited spin state equilibrium provides appreciable population of the low-spin charge transfer state: (π^*, t_{2g}^5) + Energy = (π^*, e_g^2, t_{2g}^3).

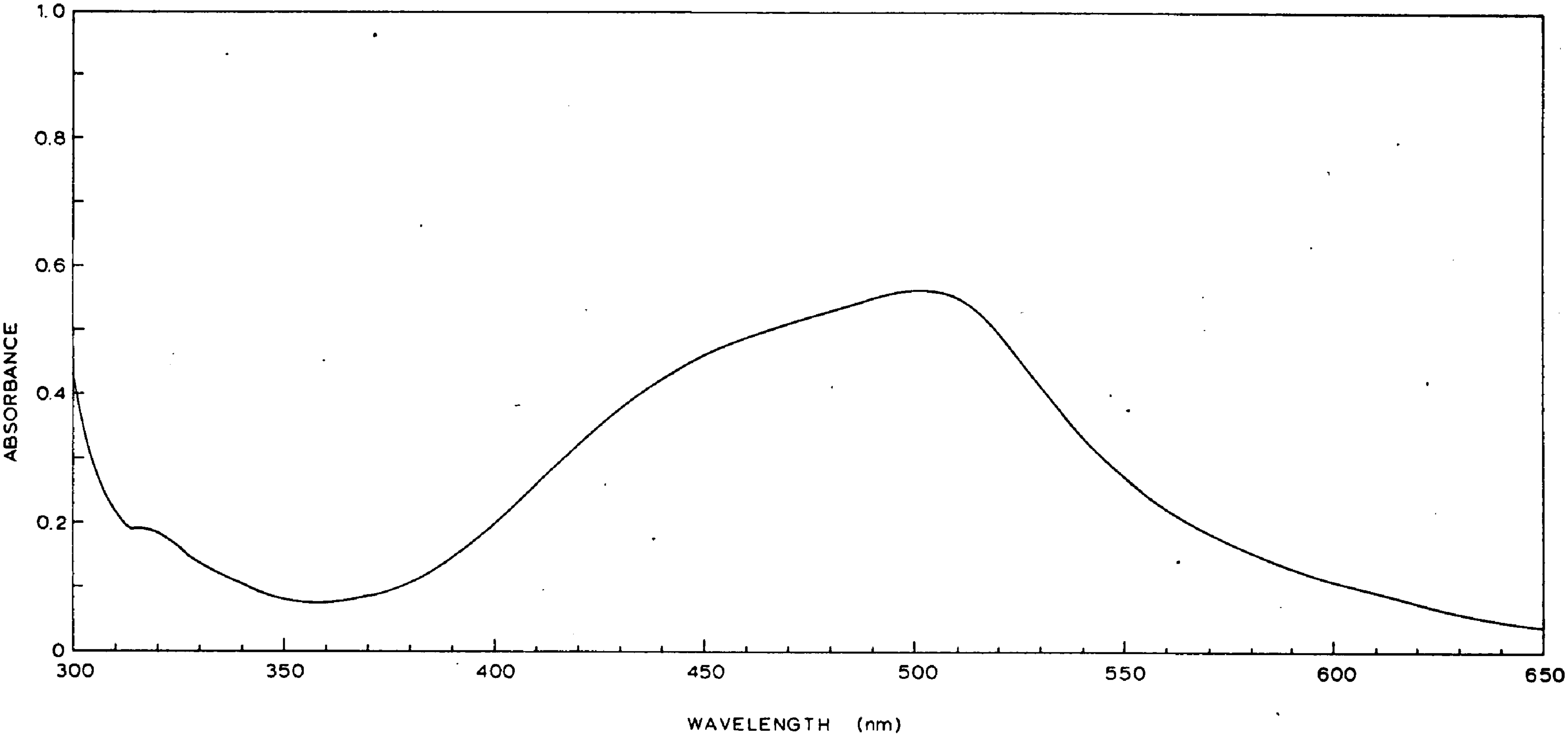


Figure 7. Absorption Spectrum of dichloro-*bis*-(1,10-phenanthroline)-ruthenium(II)

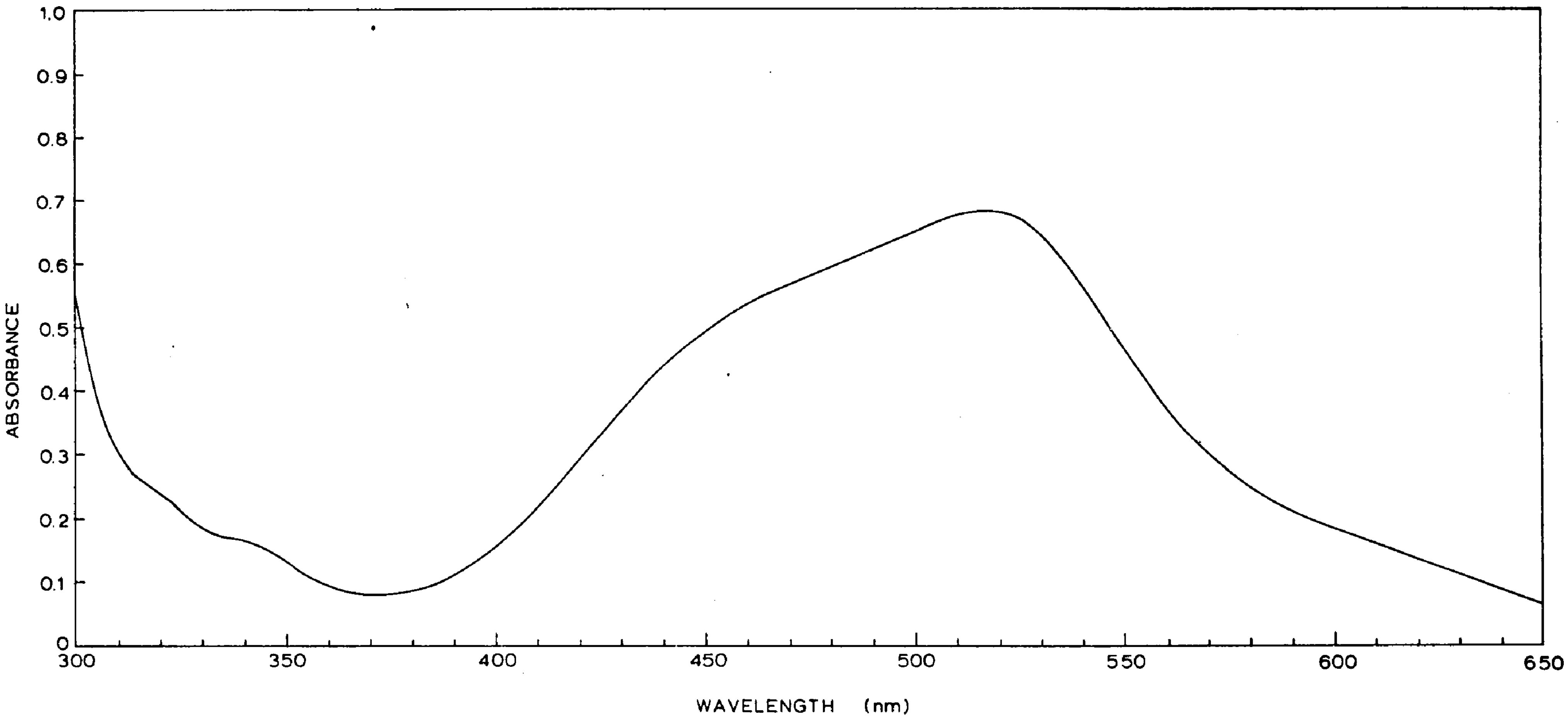


Figure 8. Absorption Spectrum of [Oxalato-*bis*-1,10-phenanthroline-ruthenium(II)]$^{2+}$

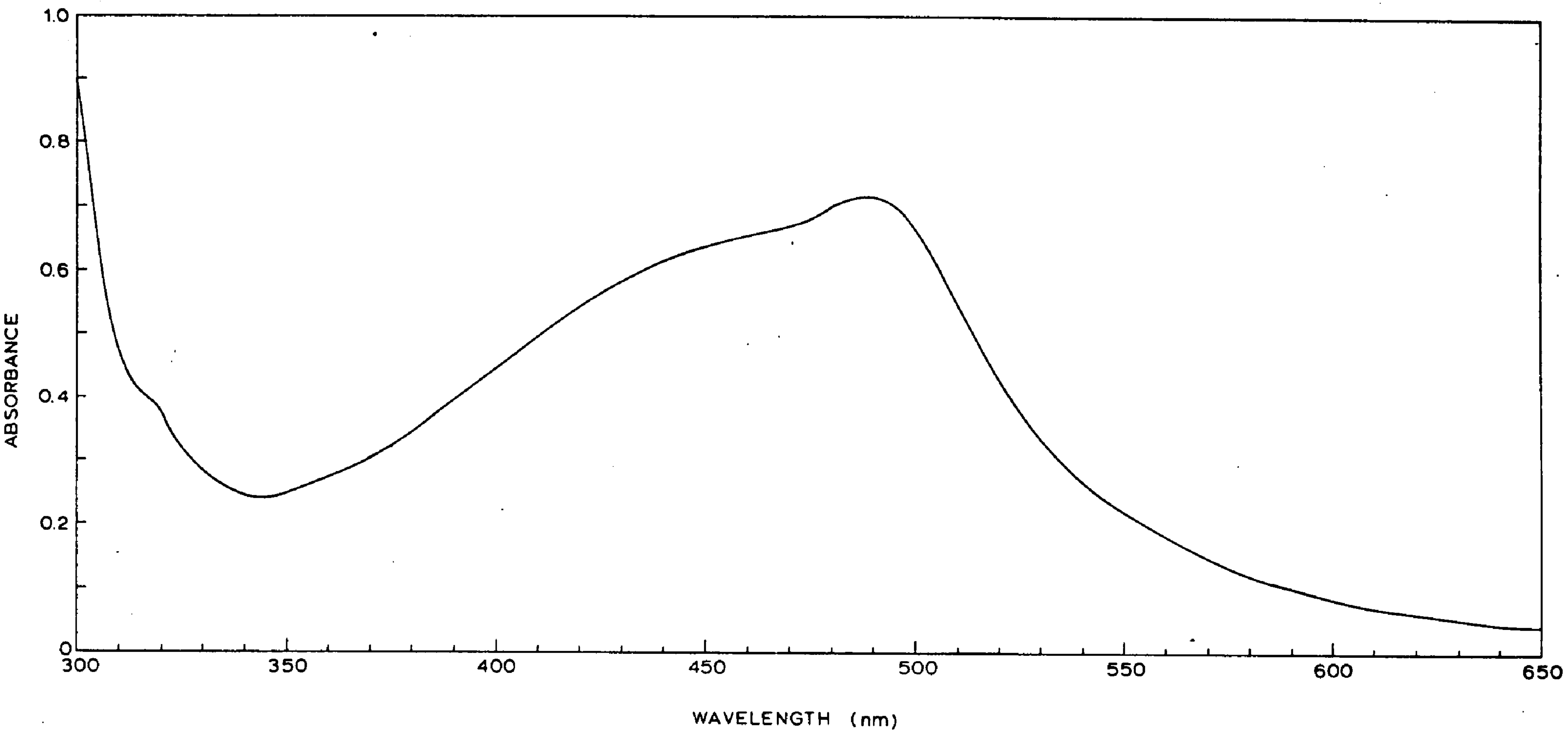


Figure 9. Absorption Spectrum of [diaquo-*bis*-1,10-phenanthroline-ruthenium(II)]$^{2+}$

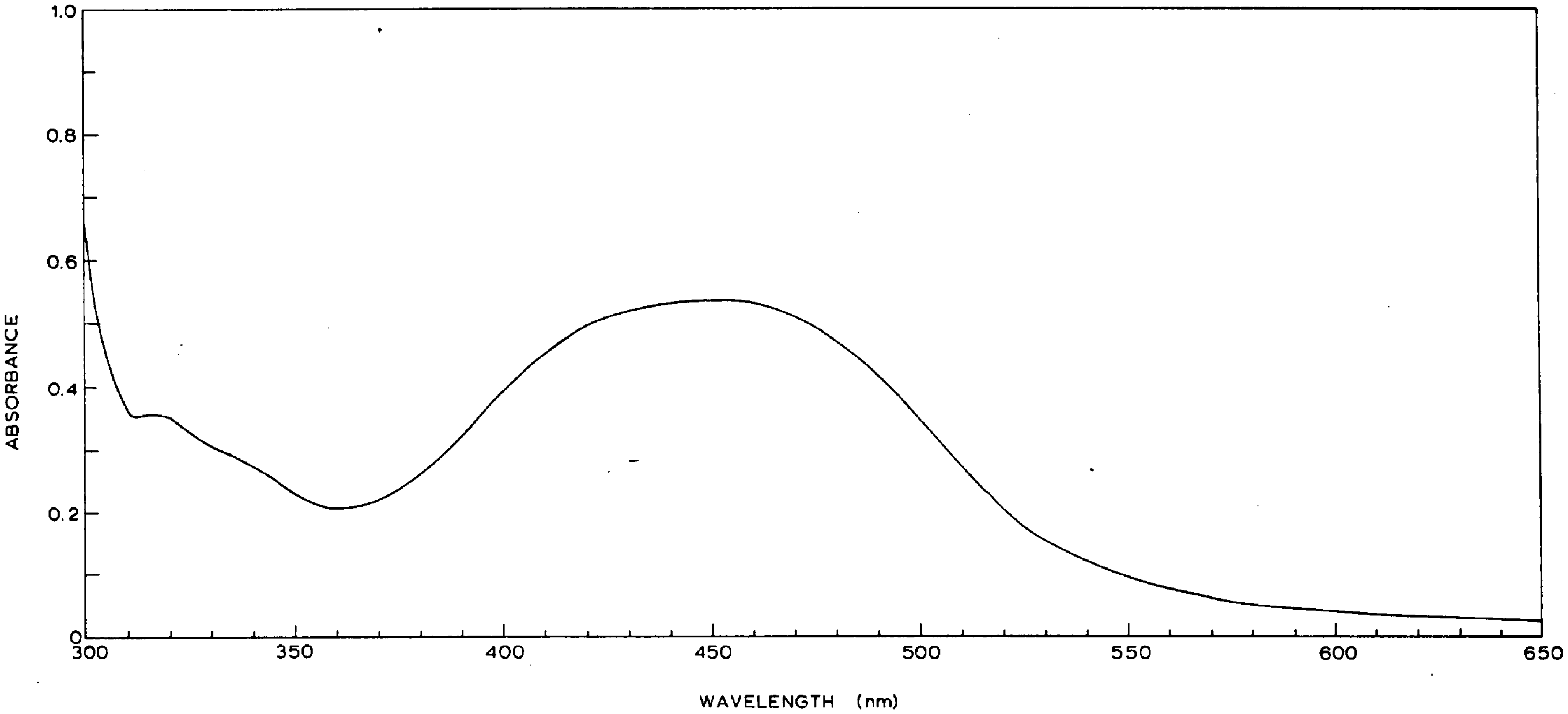


Figure 10. Absorption Spectrum of [Aquo-pyridine-*bis*-1,10-phenanthroline-ruthenium(II)]$^{2+}$

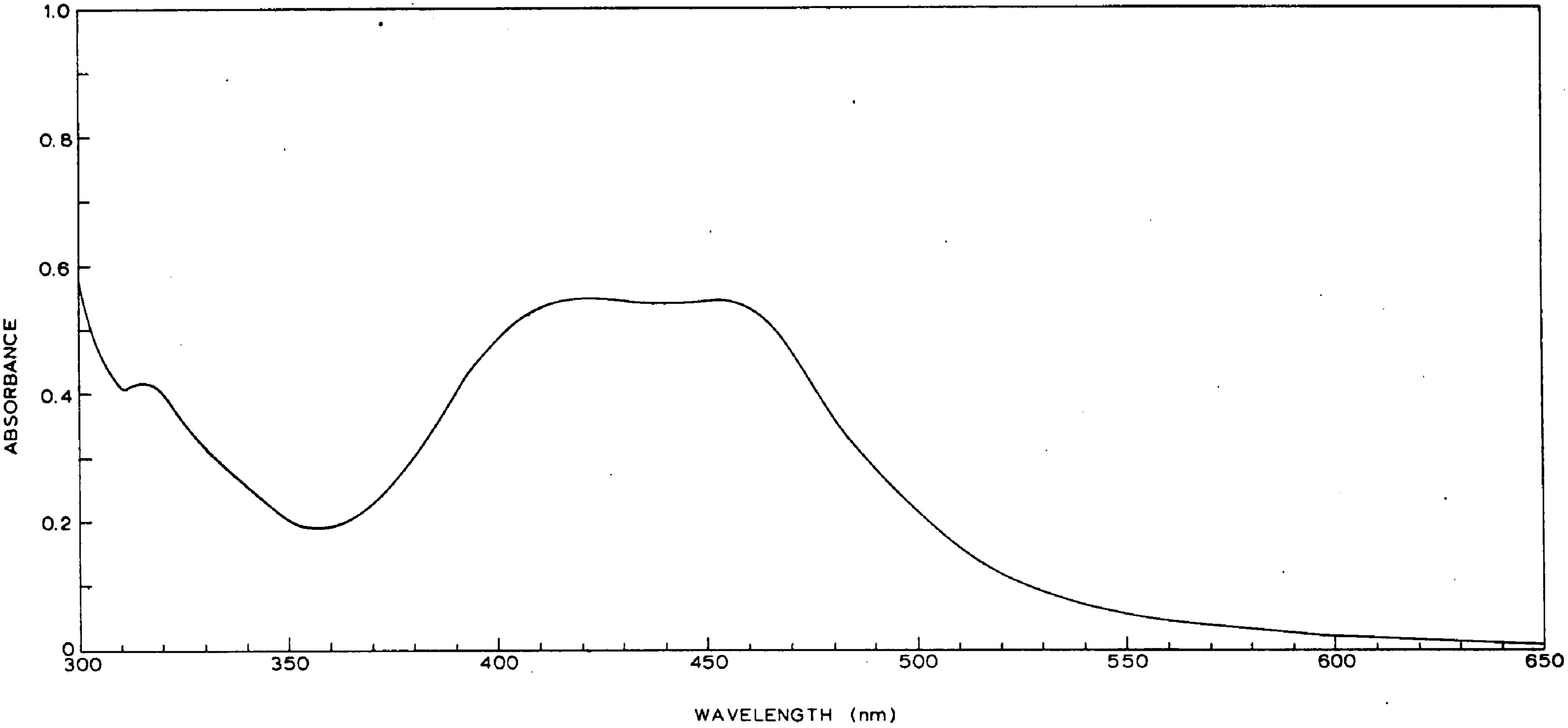


Figure 11. Absorption Spectrum of [bis-pyridine-bis-1,10-phenanthroline-ruthenium(II)]$^{2+}$

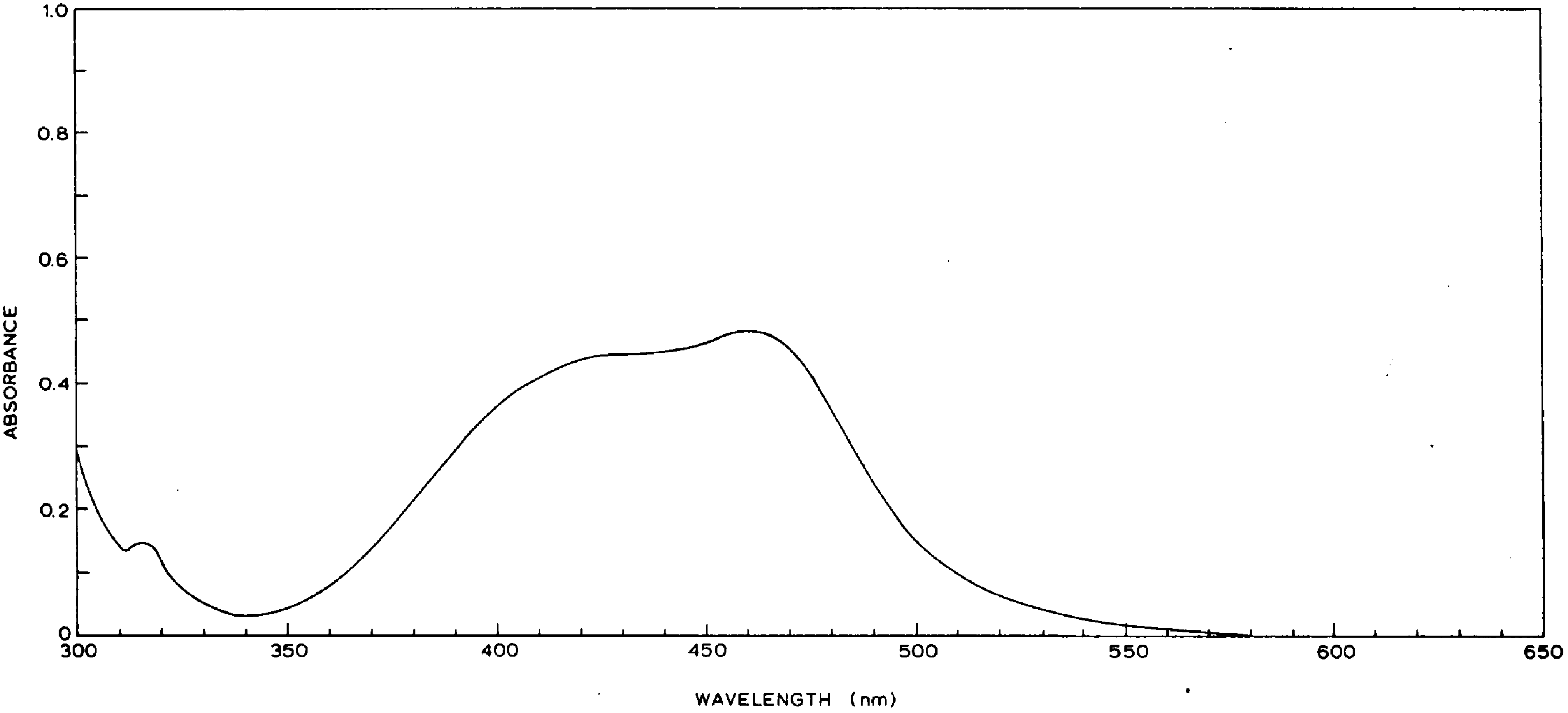


Figure 12. Absorption Spectrum of dicyano-*bis*-1,10-phenanthroline-ruthenium(II)

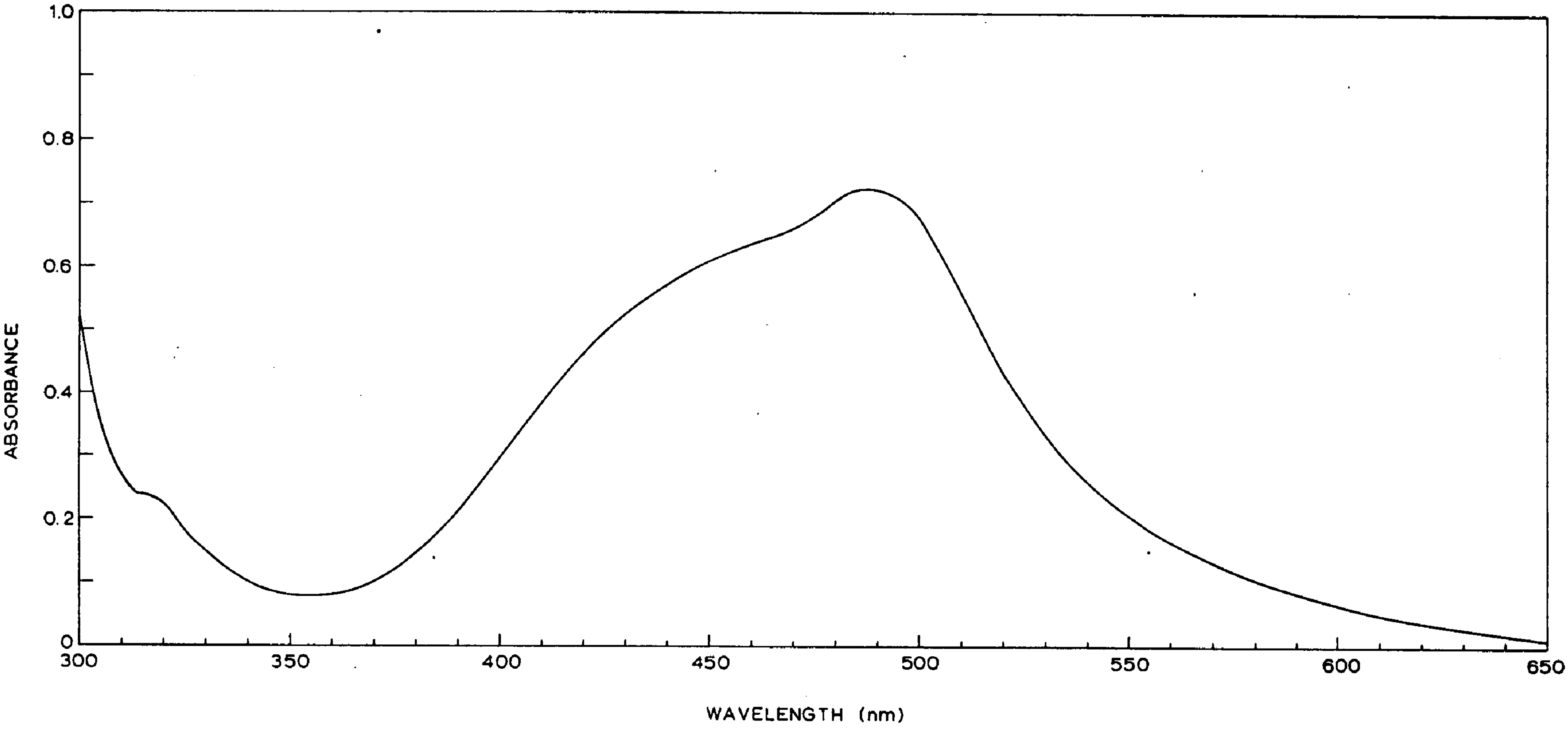


Figure 13. Absorption Spectrum of [diammine-bis-1,10-phenanthroline-ruthenium(II)]$^{2+}$

The luminescence of [diammine-bis-phen-Ru(II)]$^{2+}$ was observed to increase almost linearly with decreasing temperature. The absence of more pronounced temperature effects on its luminescence intensity is attributed to the presence of the heavy counter-ion, iodide, which increases the intersystem crossing rate constant.

More detailed consideration of the relative luminescence intensities of these chelates was not attempted. There are many factors that affect the efficiency of the luminescence processes. The relative importance of each is difficult to assess to the accuracy which would be necessary to explain the differences observed in the luminescence intensities among these chelates.

IV. FORMATION STUDY OF TRIS-(1,10-PHENANTHROLINE)-RUTHENIUM(II)

A. Introduction

The imine ligands 1,10-phenanthroline, 2,2'-bipyridine, 2,2',2"-terpyridine, and their derivatives form highly stable and intensely colored chelates with many transition metal ions; these provide the basis of numerous analytical spectrophotometric methods (79). The kinetics of formation and dissociation reactions of most of the divalent metal ions in the first Transition Row with these imines have been studied and show similar behavior. The second-order rate constant for formation of the mono complex of many of the first row transition metals is controlled by the water exchange rate of the aquated metal ion and the ligand has a minimal influence. Although fast-reaction techniques are required to study these systems due to the very rapid rates of formation, the first row transition metals have been thoroughly studied. However, there is little information on the kinetics and mechanism of the formation reactions of most ions beyond the first row of transition metals. Thus, Fe(II) ($3d^6$ electron configuration) reactions with the imine ligands have been extensively studied in contrast to those of Ru(II) ($4d^6$ electron configuration). This is somewhat surprising in view of the expected similarity of the coordination chemistry of these two metals together with the added advantage that chelate formation reactions of ruthenium(II) and most other heavy transition metal ions are quite slow and can be conveniently followed by conventional simple kinetic methods.

Brandt, et al. (12) have investigated the intermediates in the stepwise formation of the tris-(2,2'-bipyridine) ruthenium(II) ion in aqueous solution by spectrophotometry. The starting material, a mixture of about 40% $RuCl_3$ and 60% $RuCl_4$ (ruthenium chloride salt commercially available at that time) and 2,2'-bipyridine, were refluxed together in dilute H_2SO_4 (pH 2). Complex formation was reported to occur only with the Ru(III) and followed the sequence: $[Ru(III)(bipyridine)]^{3+}$, a blue species with λ_{max} = 705 nm, is formed first; it is rapidly converted to a green (λ_{max} = 630 nm) complex-$[Ru(III)(bipyridine)_2(H_2O)_2]^{3+}$, which is converted slowly to the yellow $[Ru(II)(bipyridine)_3]^{2+}$.

Refluxing the Ru(III)-Ru(IV) salt in 1 M HCl to form first the chloro complexes, then refluxing with an equimolar amount of bipyridine at pH 2 gave a red complex which they reported to be $[Ru(III)(bipyridine)_2Cl_2]^{+}$. If excess 2,2'-bipyridine was present, $[Ru(II)(bipy)_3]^{2+}$ was formed; there was no mono-bipyridine ruthenium(III) species observed in this instance. Even more unusual and interesting is the species $[Ru(IV)(bipy)_2Cl_2]^{2+}$ which was reported to be an intermediate in the conversion of $[Ru(III)(bipy)_2Cl_2]^{+}$ to $[Ru(II)(bipy)_2]^{2+}$.

The purpose of this investigation was to confirm the formation of the mono- and bis-imine species in solution and to determine the point in the chelation process at which ruthenium(III) is reduced to ruthenium(II). 1,10-Phenanthroline was chosen as the ligand because of its similarity to and because it is less volatile than 2,2'-bipyridine.

A number of ruthenium(II)-imine chelates are known to luminesce; however, ruthenium(III) is a paramagnetic ion and its chelates do not luminesce. It was therefore thought that by monitoring the luminescence of the reaction solutions, the first appearance of luminescence could be associated with the conversion of Ru(III) to Ru(II). Unfortunately it was later found that the mono- and bis-phenanthroline Ru(II) species do not luminesce unless the remaining coordination sites are occupied by ligands that produce stronger ligand fields than those provided by Cl^- or H_2O. Under the conditions of these experiments only the tris-phenanthroline Ru(II) chelate would exhibit the characteristic red-orange charge transfer luminescence. This discovery precluded the possibility of identifying unequivocally the point at which Ru(III) is reduced to Ru(II) and eventually led to a study of the dependence on the ligand field strength of X of the charge transfer luminescence of $Ru(II)(phen)_2X_2$ compounds. The following discussion is therefore limited to a presentation and consideration of the data collected during the formation of the tris-1,10-phenanthroline Ru(II) species together with some suggestions for future study.

B. Experimental

Ruthenium(III) trichloride hydrate (Alfa Inorganics, Inc.), 1,10-phenanthroline, and *tris*-1,10-phenanthroline ruthenium(II) dichloride (both from G. F. Smith Chemical Company) were used without further purification.

The complexes in this section were prepared using procedures given in the literature, the references are cited in the text of the Results and Discussion Section. Oxidation of Ru(II)-imine chelates to obtain the spectrum of the corresponding Ru(III)-imine chelate was accomplished by treatment of an acidic solution (*ca*. 0.9 N H_2SO_4, pH *ca*. 1) of the chelate with lead dioxide (J. T. Baker).

A stock Ru(III) solution was prepared by dissolving *ca*. 0.15 g of $Ru(III)Cl_3.xH_2O$ in 50 ml of distilled water. The pH of the solution was adjusted to *ca*. 1 with sulfuric acid to prevent hydrolysis of the ruthenium. The exact amount of ruthenium in this solution was determined spectrophotometrically using 1,10-phenanthroline (80). The working solution was prepared by a 1:10 dilution of the stock solution, pH adjusted to *ca*. 1.

C. Results and Discussion

The reaction of Ru(III), (*ca*. 5 x 10^{-2} m*M*), with 1,10-phenanthroline at pH 2 was followed at ligand-to-metal ratios of 0.5, Figure 14, and 6.0, Figure 15. The solution is initially colorless or very faintly yellow, due to the extension of the long wavelength tail of the very intense ligand $\pi^* \leftarrow \pi$ bands (λ_{max} ca. 285 nm) into the visible. As the solutions are heated they become a pale blue (an absorption band appears with λ_{max} ca. 715 nm); this color rapidly increased in intensity and a new absorption band (λ_{max} ca. 635 nm) replaced the previous one at 715 nm.

If the ligand-to-metal ratio is low, L/M = 0.5, Figure 14, the formation of the tris-imine Ru(II) species is seriously inhibited and the reaction proceeds very slowly and is not complete. This is evidenced by the absorption spectrum ($\pi^* \leftarrow d$ band characteristic of Ru(II) imines, λ_{max} ca. 400-450 nm - Figures 16-18, is relatively weak and poorly defined) and by the weak luminescence, even after 39 hours of refluxing. The solution color changes only slightly during this time, becoming greenish-blue.

In the presence of excess ligand the chelation reaction occurs more rapidly and while the 715 nm band is observed briefly, it is transitory and very weak. The absorption band at 635 nm which appears during the early stages of the reaction diminishes in intensity only after extensive refluxing (Figure 15, L/M = 6, curves 3, 4 and 5). The blue color of the solution thus rapidly turns to a green which becomes more and more yellow due to the formation of the Ru(II)-phenanthroline species ($\pi^* \leftarrow d$ band at λ_{max} ca. 450 nm which

Figure 14

Absorption Intensity as a Function of Time for the Reflux of a Solution of Ruthenium(III)(1×10^{-1} m$\underline{M}$) and 1,10-Phenanthroline (5×10^{-2} m$\underline{M}$) at pH2, L/M *ca*. 0.5

Curve[a]	Time of Heating	Percent[b] $[Ru(II)(phen)_3]^{2+}$	I_L^c
1	15 min	10	0
2	35 min	11	0
3	1 hr	13	0
4	2 hr	12	.0012
5	39 hr	24	.024

[a] 1.00-cm. cells

[b] Based on ε^{450} of $[Ru(II)(phen)_3]^{2+}$ of 1.8×10^4

[c] I_L excited at 435 nm and measured at 590 nm relative to a fluorescence intensity of 2.0 arbitrary scale units for a 1.0 ppm quinine sulfate solution in 0.10 $\underline{N}$ H_2SO_4 excited by 365 nm radiation and showing fluorescence at 450 nm.

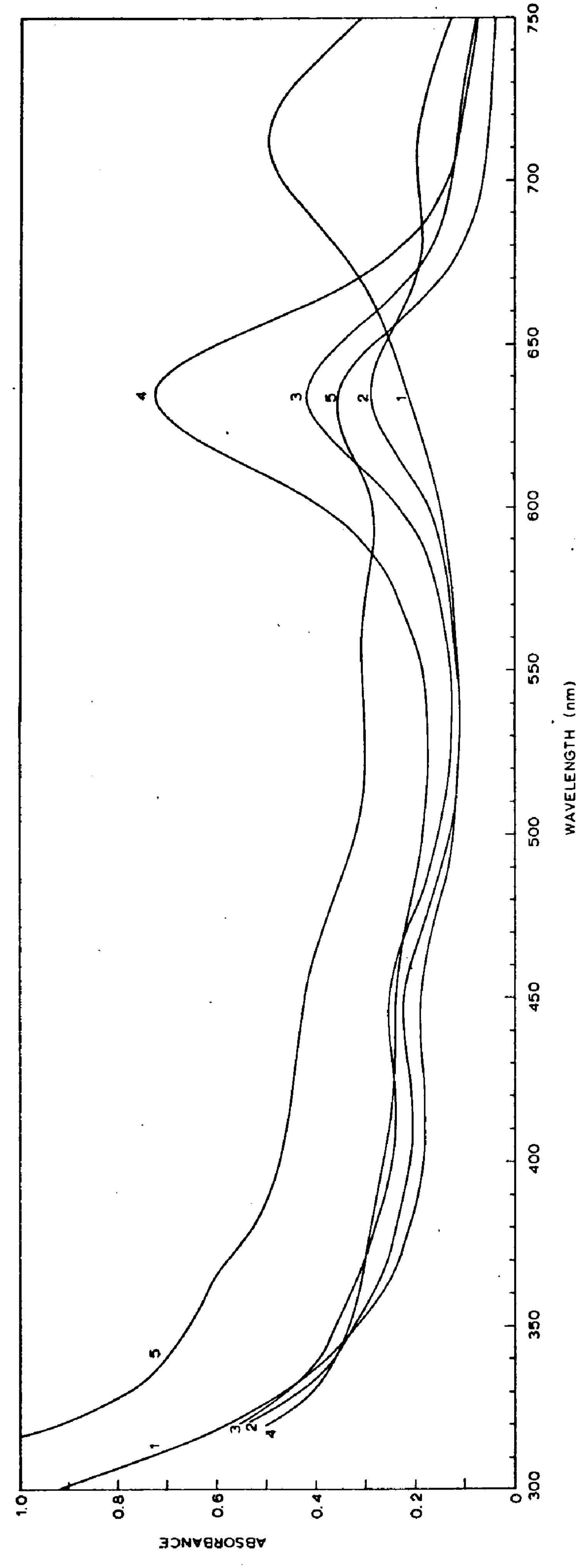

ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0
WAVELENGTH (nm)
300
350
400
450
500
550
600
650
700
750
1
2
3
4
5

Figure 15

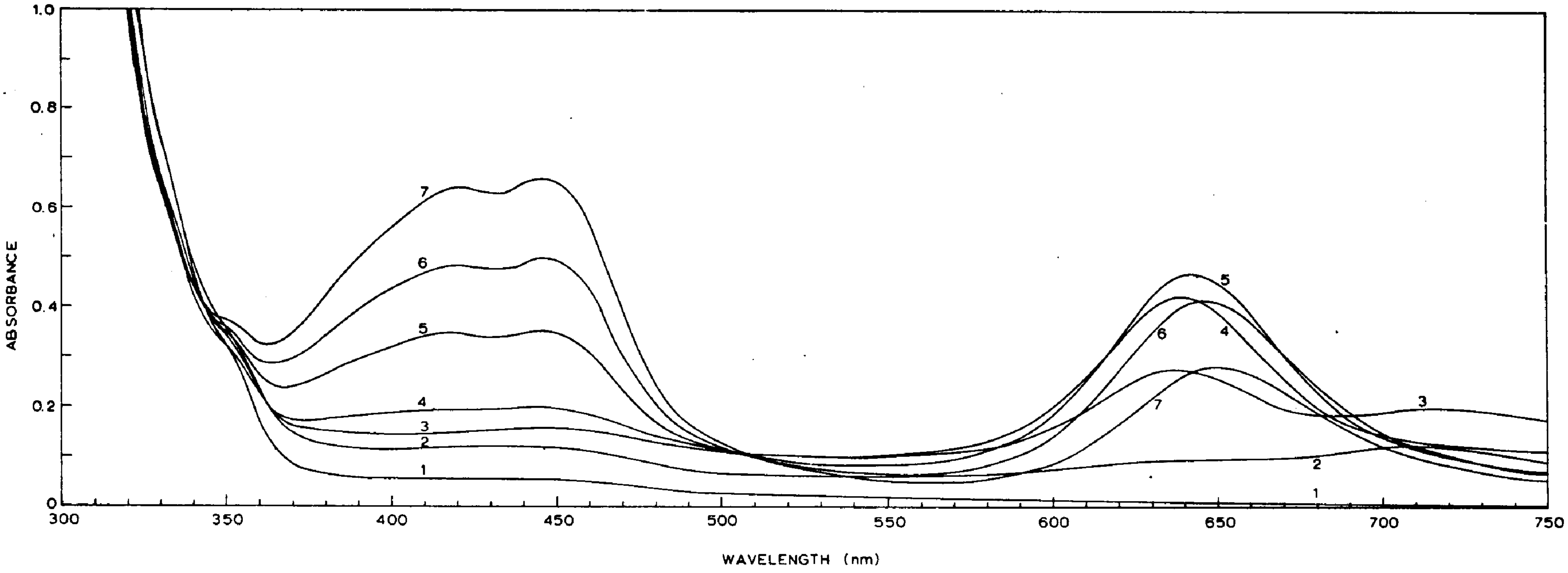
Absorption Intensity as a Function of Time for the Reflux of a Solution of Ruthenium(III)(5 x 10^{-2} m$\underline{M}$) and 1,10-Phenanthroline (30 x 10^{-2} m$\underline{M}$) at pH2, L/M *ca*. 6

Curve[a]	Time of Heating	Percent[b] $[Ru(II)(phen)_3]^{+2}$	I_L^c
1	0 min	4	0
2	15 min	11	0
3	1 $\frac{3}{4}$ hr	18	.021
4	3 $\frac{3}{4}$ hr	20	.17
5	10 $\frac{3}{4}$ hr	34	-
6	25 $\frac{3}{4}$ hr	54	-
7	46 $\frac{1}{2}$ hr	72	-

[a] 1.00-cm. cells

[b] Based on ε^{450} of $[Ru(II)(phen)_3]^{2+}$ of 1.8 x 10^4

[c] I_L excited at 435 nm and measured at 590 nm relative to a fluorescence intensity of 2.0 arbitrary scale units of a 1.0 ppm quinine sulfate solution in 0.10 $\underline{N}$ H_2SO_4 excited by 365 nm radiation and showing fluorescence at 450 nm.



ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0
300
350
400
450
500
550
600
650
700
750
WAVELENGTH (nm)
7
6
5
4
3
2
1
5
6
4
7
3
2
1

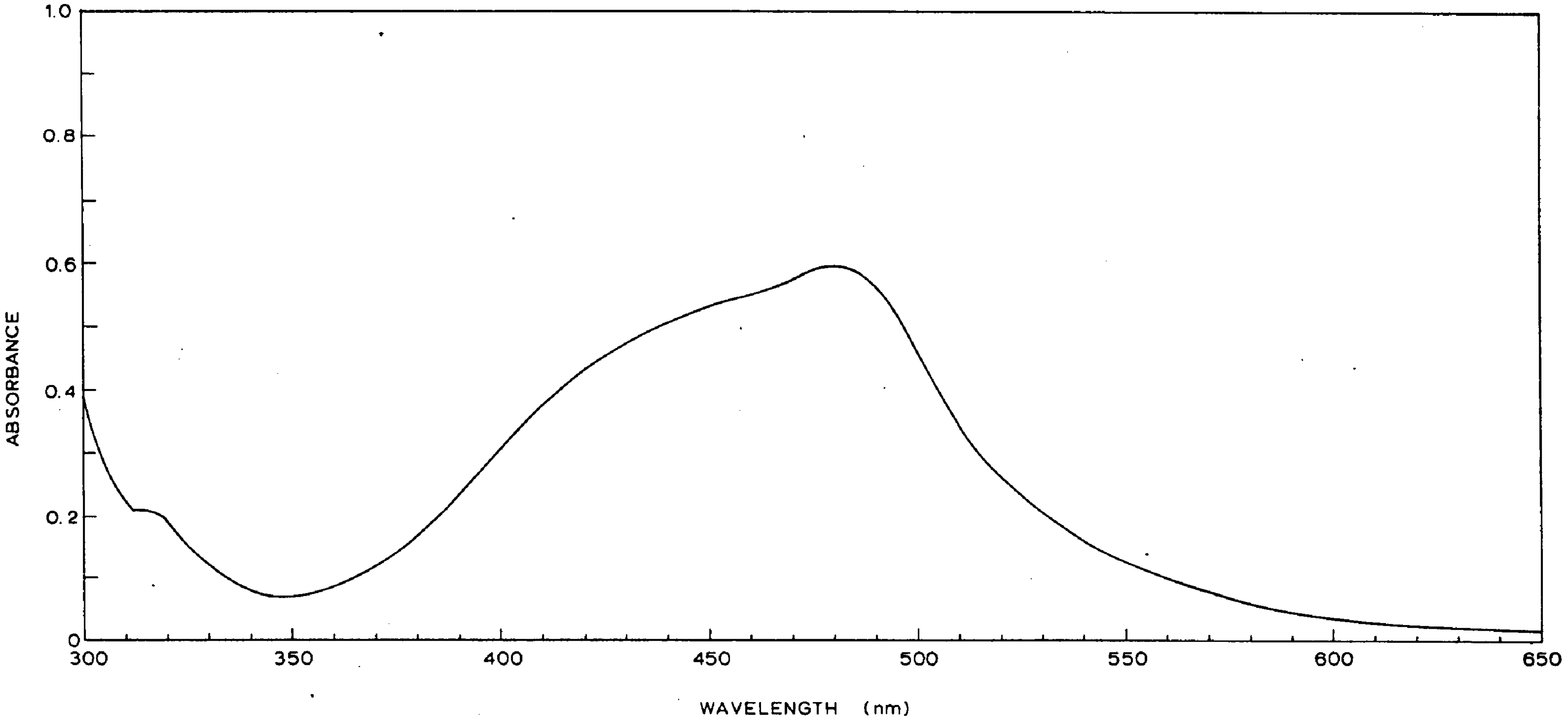


Figure 16. Absorption Spectrum of Ru(II)(phen)$_3$Cl$_2$ (0.033 m<u>M</u> in absolute ethyl alcohol)

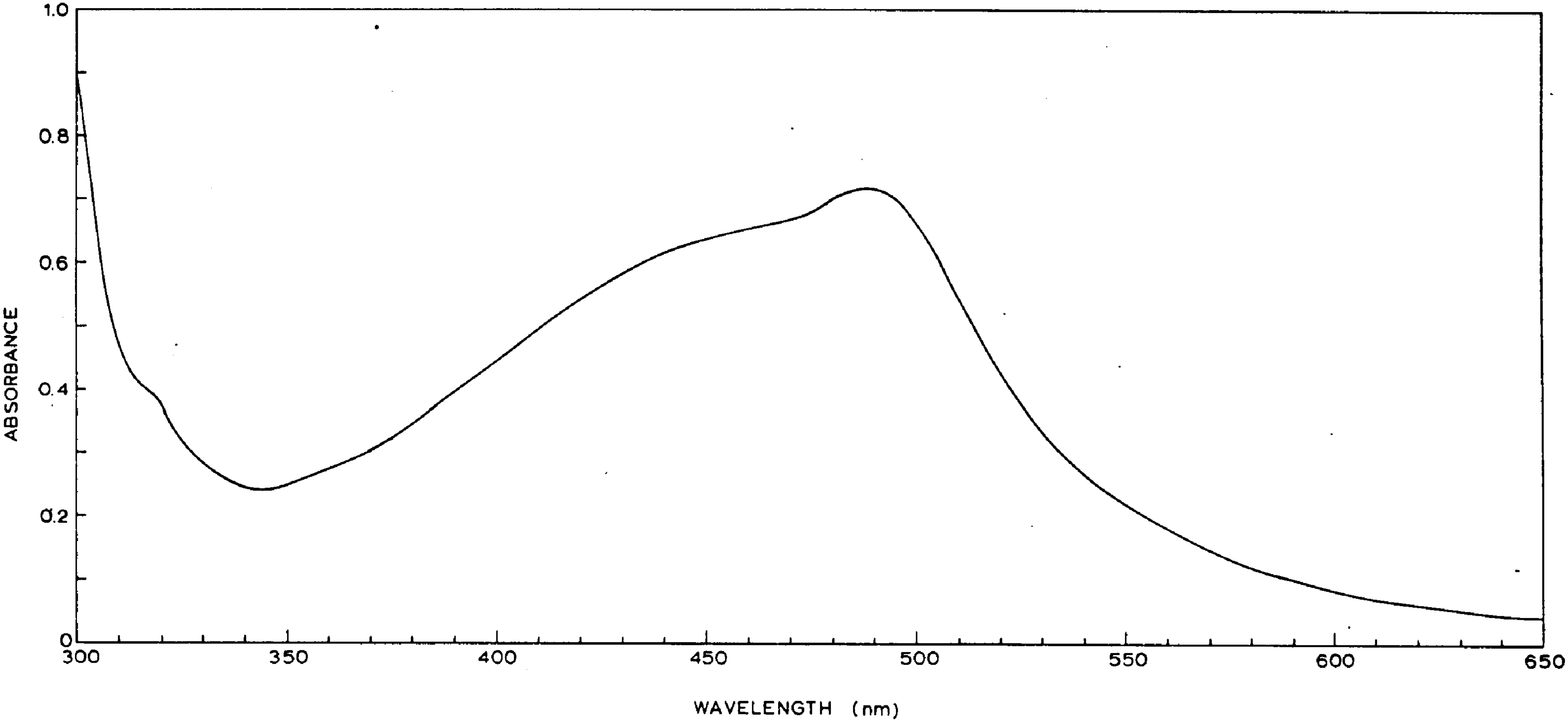


Figure 17. Absorption Spectrum of $[Ru(II)(phen)_2(H_2O)_2]^{2+}$ (0.14 m$\underline{M}$ in absolute ethyl alcohol)

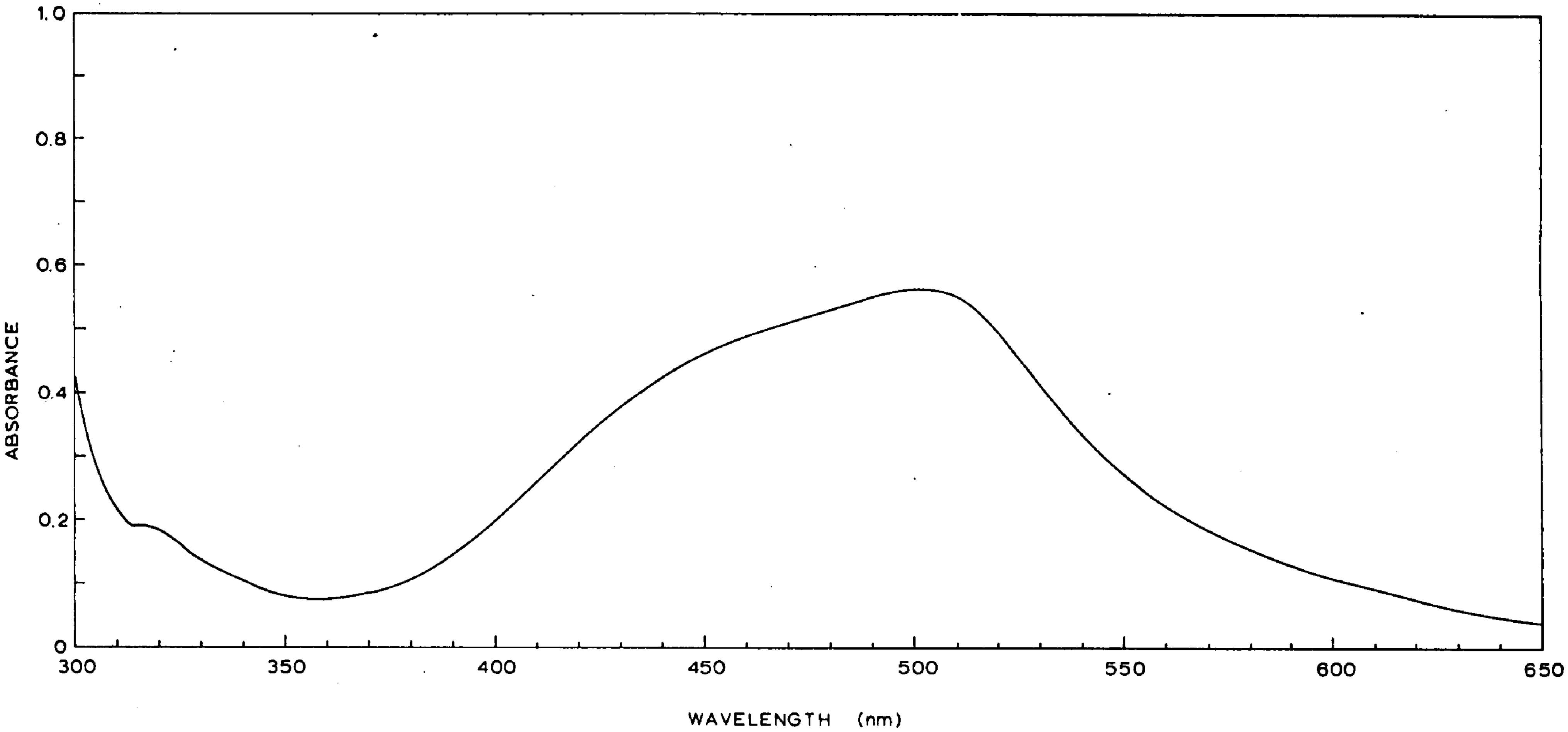
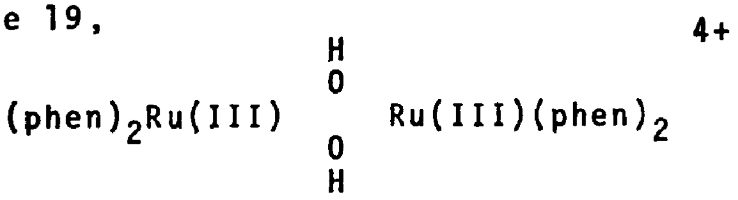


Figure 18. Absorption Spectrum of Ru(II)(phen)$_2$Cl$_2$ (0.20 m<u>M</u> in absolute ethyl alcohol)

becomes the major visible band throughout the later stages of the reaction process: curves 6 and 7 in L/M = 6 - Figure 15). The presence of tris-1,10-phenanthroline Ru(II) is confirmed by the appearance and increasing intensity of the characteristic red-orange luminescence of the tris-phen Ru(II) species.

The absorption bands parallel those observed by Brandt et al. in their work using 2,2'-bipyridine and probably result from analogous species. To aid in the identification of the species present a number of compounds suspected to be intermediates in this reaction sequence were prepared; their uv-visible absorption spectra were compared with the spectra obtained in the formation study.

The spectrum of tetrakis-phenanthroline-μ-diol Ru(III), Figure 19,



$$(\text{phen})_2\text{Ru(III)}\begin{matrix}\text{H}\\ \text{O}\\ \\ \text{O}\\ \text{H}\end{matrix}\text{Ru(III)(phen)}_2{}^{4+}$$

strongly resembles that of the second product (λ_{max} ca. 635 nm) which is formed in the Ru(III)-phen reaction and gives rise to the deep blue color. The compound absorbing at 715 nm may be a bridged diol containing fewer coordinated phenanthroline molecules. The molar absorptivities of the 715 nm and 635 nm bands in the reaction solutions are ca. 7×10^3. These bands are much too intense to be d-d in origin and are tentatively assigned as ligand-to-metal,

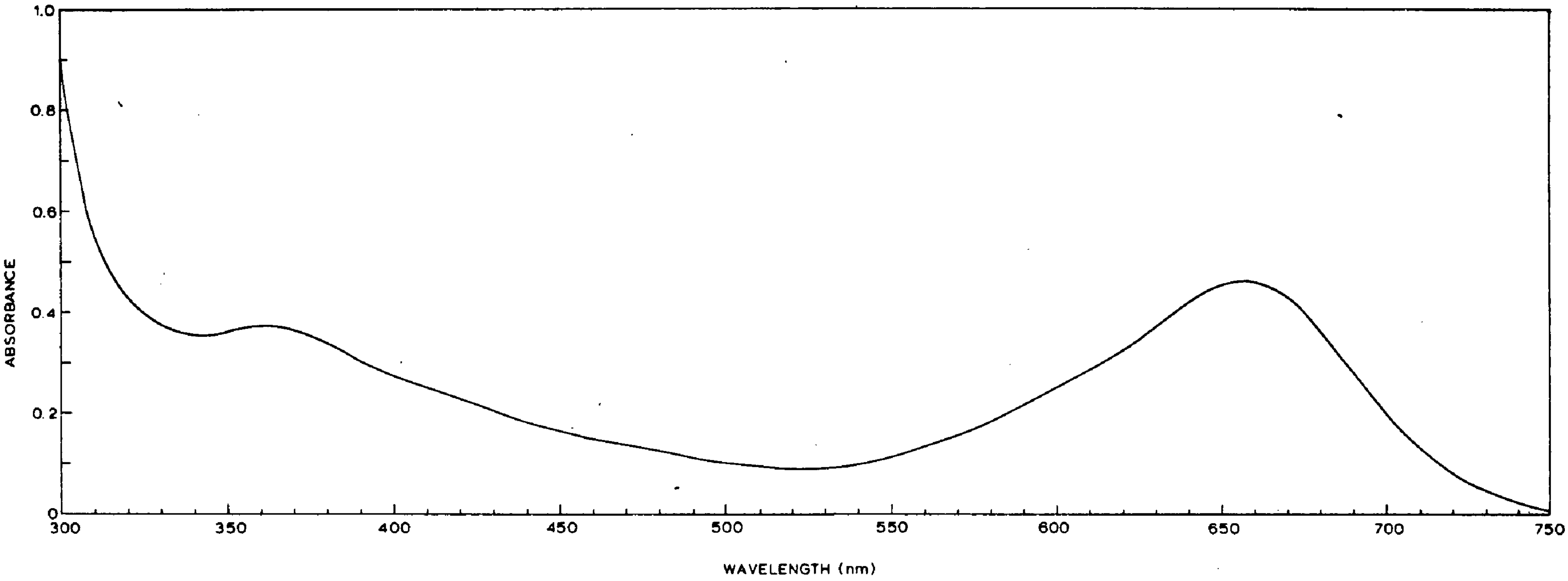


Figure 19. Absorption Spectrum of [<u>tetrakis</u>-phen-μ-diol-Ru(III)]$^{4+}$ in absolute ethyl alcohol

$d^* \leftarrow \pi$, transitions. Studies of the $d^* \leftarrow \pi$ charge transfer spectra of the chloro and bromo complexes of Ru(III) show complex bands occurring in the visible and uv regions with molar extinction coefficients of ca. 2 x 10^3 (22,81,82).

The identification of Ru(II)$(phen)_2Cl_2$, Figure 18, or $[Ru(II)(phen)_2(H_2O)_2]^{2+}$, Figure 17, in the reaction mixture is difficult due to the similarity of their absorption spectra to that of the final product, $[Ru(II)(phen)_3]^{2+}$, Figure 16. However, because $[Ru(II)(phen)_3]^{2+}$ is believed to be the only luminescent species in these reaction solutions, its rate of formation can be set equal to the rate of increase in the luminescence intensity with time.

All Ru(II)-phen chelates show a $\pi^* \leftarrow d$ charge transfer band at λ_{max} ca. 450 nm (Figures 16-18) having of ca. 3 x 10^3; the Ru(III) species are transparent or only weakly absorbing at 450 nm, Figures 15, 19, 20, 21. Thus, by also following the intensity of the $\pi^* \leftarrow d$ absorption band at 450 nm, the rate of formation of all Ru(II)-phen species can be determined. Figure 22 shows the relative rates of formation of $[Ru(II)(phen)_3]^{2+}$ and of the Ru(II)-phen species. The nearly identical initial rates suggest that the only important Ru(II)-phen species present in the reaction sequence is the final product $[Ru(II)(phen)_3]^{2+}$ - i.e., reduction of Ru(III) occurs after (or concurrent with) the third chelation step.

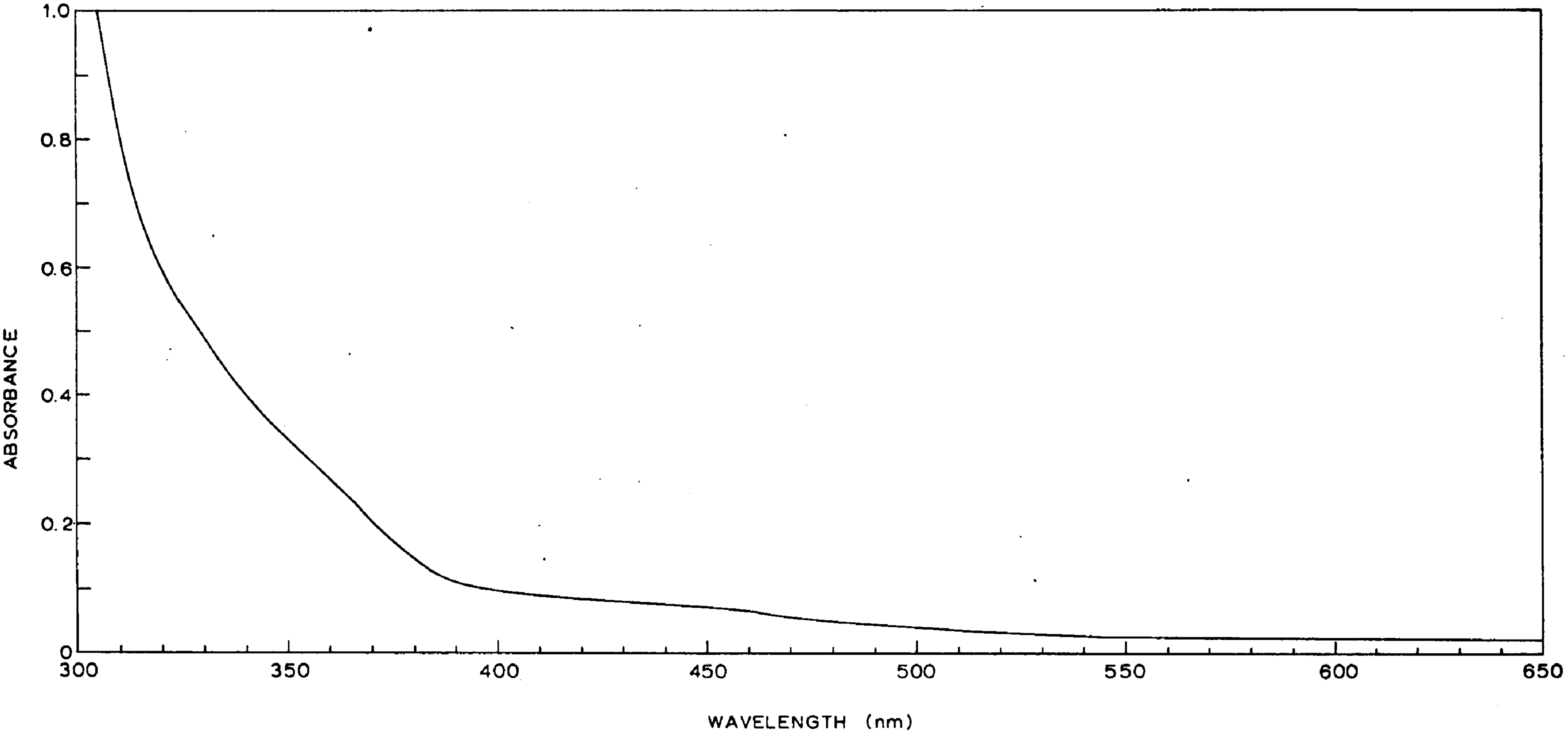


Figure 20. Absorption Spectrum of $[Ru(III)(phen)_3]^{3+}$ in absolute ethyl alcohol

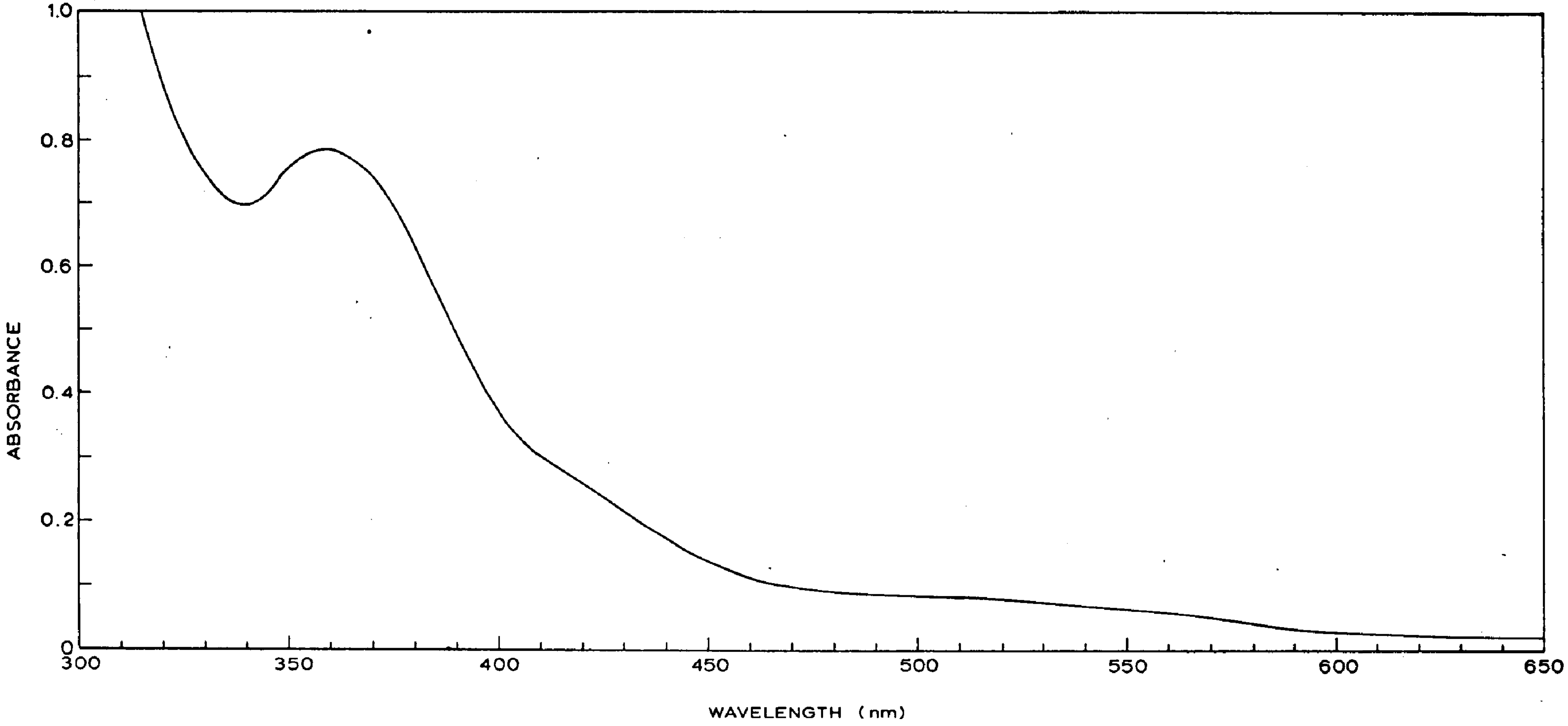


Figure 21. Absorption Spectrum of $[Ru(III)(phen)_2]^{3+}$ in absolute ethyl alcohol

Figure 22

($\pi^* \leftarrow d$) Absorption and Luminescence Intensities vs. Reflux Time for Solutions of Ru(III) (5×10^{-2} m*M*) and 1,10-Phenanthroline (30×10^{-2} m*M*) at pH2, L/M *ca*. 6

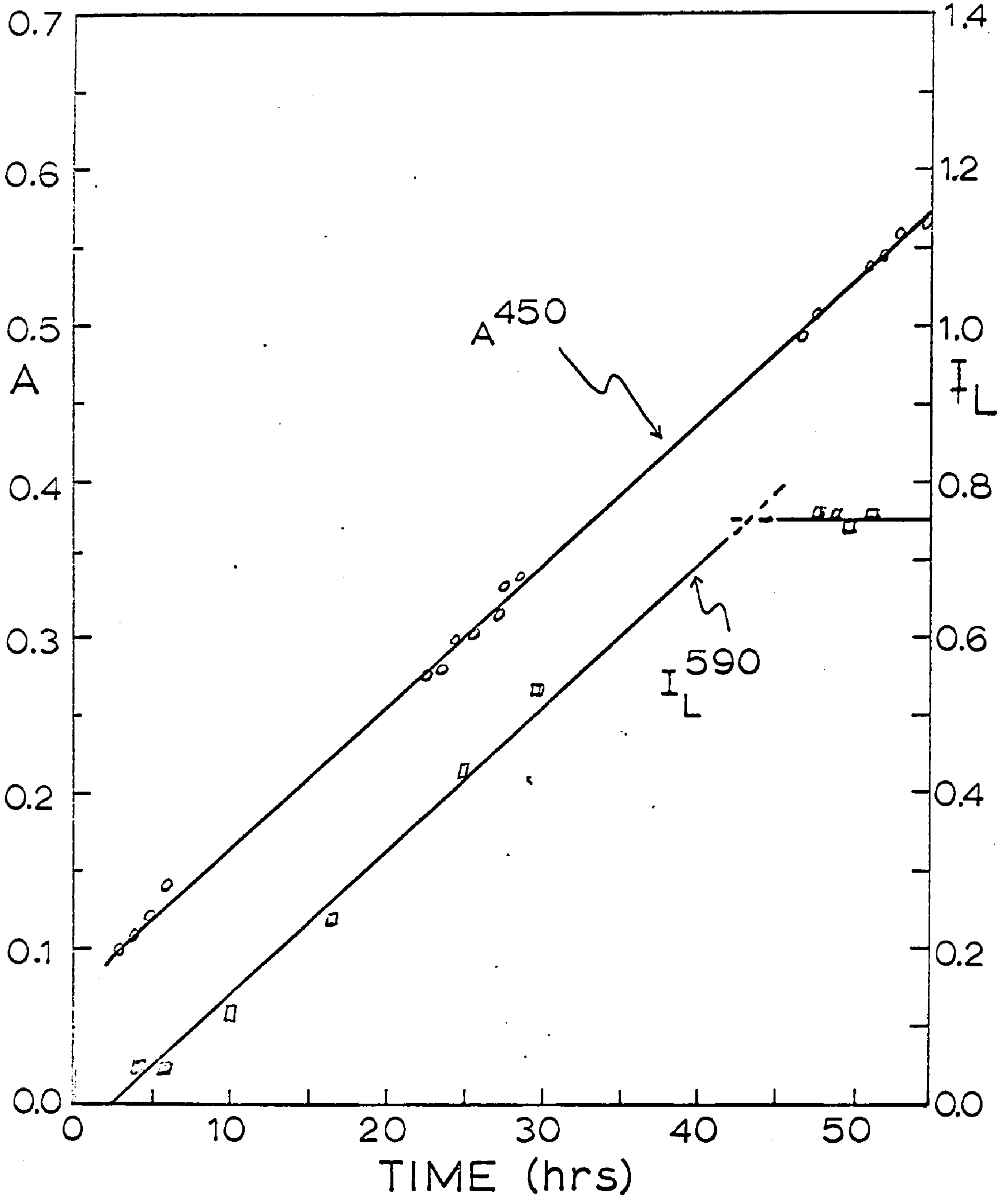

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
A
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
I_L
A^{450}
I_L^{590}
0
10
20
30
40
50
TIME (hrs)

TABLE VII

Absorption and Luminescence Intensity as a Function of Time for the Reflux of a Solution of Ruthenium(III)(5 x 10^{-2} m<u>M</u>) and 1,10-Phenanthroline (30 x 10^{-2} m<u>M</u>) at pH2, L/M *ca*. 6

Time of Heating	I_L[a]	A^{450}	Percent Formation of $[Ru(II)(phen)_3]^{2+}$
0	0	.027	0
15 min	0	.070	0
30 min	0	.067	0
1 hr	.0002	.098	0
3 hr	.015	.100	17
5 hr	.051	.122	21
7 hr	.063	.161	27
22.5 hr	.35	.275	47
25.5 hr	.40	.302	51
27.5 hr	.41	.334	57
30.5 hr	.69	.390	66
46.5 hr	.82	.496	84
48.5 hr	.76	.510	87
51.5 hr	.81	.547	93
54.5 hr	.68	.567	96
∞[b]	.61	.588	100

[a] I_L excited at 435 nm and measured at 590 nm relative to a fluorescence intensity of 2.0 arbitrary scale units of a 1.0 ppm quinine sulfate solution in 0.10 <u>N</u> H_2SO_4 excited by 365 nm radiation and showing fluorescence at 450 nm.

[b] Addition of hydroxylamine hydrochloride and reflux 30 minutes.

In summary it appears that the first species formed when a solution of Ru(III) and 1,10-phenanthroline are heated together at pH02 may be a bridged diol (containing an unknown number of phenanthroline ligands). This is rapidly converted to tetrakis-phenanthroline-μ-diol ruthenium(III). The follow-up steps in reaching the final complex, $[Ru(II)(phen)_3]^{2+}$, are not known for certain, however, there are two possibilities: 1) the bridged diol may break apart and add the third phenanthroline to give $[Ru(III)(phen)_3]^{3+}$ which could then be reduced by a phenanthroline molecule to form $[Ru(II)(phen)_3]^{2+}$, or 2) the reduction step may precede the addition of the final ligand, i.e., the bridged diol may be reduced to give $[Ru(II)(phen)_2]^{2+}$ followed rapidly by the final ligation step to yield $[Ru(II)(phen)_3]^{2+}$. The spectrum of $[Ru(III)(phen)_3]^{3+}$, Figure 20, does not exhibit any transitions in the visible region with ε ca. 10^2 and it is therefore difficult to determine its presence in the reaction mixture based on the available spectral data.

Reduction to $[Ru(II)(bipyr)_2]^{2+}$ followed by rapid addition of the final ligand was proposed by Brandt based on his observations that in the presence of a reducing agent such as sodium sulfite, $[Ru(II)(bipyr)_3]^{2+}$ begins to form immediately with no indication of an intermediate species. This evidence is not conclusive however, and may only illustrate the already known greater lability of ruthenium(II) over ruthenium(III) (83).

No attempt was made to clarify the reaction system when the Ru(III)-Ru(IV) salt was boiled with 1 M HCl to form the chloro complexes prior to being refluxed with the 2,2'-bipyridine. This deserves further study and may provide additional information to support the proposed reaction intermediates in the first case. Brandt's failure to observe any evidence for a mono-bipyridine Ru(III) species may be due to an inability of the complex to form a bridged chloro species. The red species observed was reported to be $[Ru(III)(bipy)_2Cl_2]^+$ and resembled a concentrated solution of $[Ru(III)(phen)_2Cl_2]^+$ which was prepared in this laboratory. The presence of $[Ru(IV)(bipy)_2Cl_2]^{2+}$ is very doubtful as well as its one step conversion to $[Ru(II)(bipy)_3]^{2+}$.

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His publications are:

1. "Thorium(IV)-8-Quinolinol Complexes - Re-examination of their Composition", with William E. Ohnesorge, Anal. Chem. 42, 504, (1970).
2. "Thorium(IV)-8-Quinolinol Complexes - Re-examination of their Composition", with William E. Ohnesorge, 4th Middle Atlantic Regional Meeting of the American Chemical Society, Washington, D.C., February 14, 1969.