On the basis of inductive effect alone, one would predict that the order of increasing rates should be py < β-CH_3-py < γ-CH_3-py. However, models show that the $[Co(\beta\text{-}CH_3\text{-}py)_4Cl_2]^+$ complex suffers from greater steric strain than either of the other two complexes. This additional steric acceleration may be responsible for the observed order of py < γ-CH_3-py < β-CH_3-py. Steric factors are also believed to account for the fact that *trans*-$[Copy_4Cl_2]^+$ hydrolyzes with a half-time of 23 hr. at 25°, whereas *trans*-$[Codipy_2Cl_2]^+$ reacts with water within a fraction of a second. A consideration of molecular models shows that the pyridine complex is readily constructed provided the four planar pyridines are pitched at an angle about the cobalt like the blades of a propeller. It is impossible to bring pairs of these pyridines into the same plane, as is required for the construction of the model of the 2,2′-dipyridyl complex. Still another contribution to this more rapid rate of reaction might be a greater stabilization of the reaction intermediate through resonance of the 2,2′-dipyridyl complex compared to the pyridine compound.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

The Structure and Characteristics of the Fluorescent Metal Chelates of o,o′-Dihydroxyazo Compounds[1]

BY DONALD C. FREEMAN, JR., AND CHARLES E. WHITE

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A series of compounds has been synthesized and investigated in order to determine the characteristics of structure and bond type necessary for the formation of fluorescent chelates. The parent type of structure for the compounds in this series is that of *o,o′*-dihydroxyazobenzene. Some modifications of this basic configuration such as the bis-salicylidenediamines, salicylidene-*o*-aminophenols, and salicylaldehyde azines were also studied. Both non-aqueous N,N-dimethylformamide and 34% N,N-dimethylformamide in water were found to be excellent solvents for fluorescent chelation reactions. The bonds between the metal ion and the chelating agent were found to be primarily ionic in character. Transition elements do not form fluorescent chelates with this type of compound. A strong dependence of fluorescence intensity on the size of the metal ion was observed. The acidity of the medium necessary for maximum fluorescence was found to be a critical but predictable factor.

Introduction

Non-fluorescent organic compounds capable of forming fluorescent chelates with metal ions in solution have been shown to be of considerable value as analytical reagents. The aim of this work was to determine some of the characteristics of the structural configuration and bond type necessary for fluorescence in metal chelates of the *o,o′*-dihydroxyazo compounds.

Experimental

Apparatus.—A fluorometer with some of the units similar to those described by Fletcher and Warner[2] was constructed in the authors' laboratory. The exciting source was a H100BL4 mercury vapor lamp and the measuring unit consisted of a 1P28 electronmultiplier phototube attached to an R.C.A. WV-84A ultra-sensitive microammeter. The sample holder was designed to accommodate 25-ml. glass stoppered test-tubes or square cuvettes. Excellent linearity of response was obtained throughout the visible spectrum. A Beckman DU spectrophotometer equipped with an electronmultiplier phototube was used for absorption measurements.

Reagents.—All inorganic reagents used were C.P. grade or equivalent. Distilled water was obtained from a Barnstead still. The presence in distilled water of traces of aluminum from the piping necessitated redistillation in glass for the most sensitive applications. Water purified by ion exchange is undesirable for fluorometric work since it may contain fluorescent impurities.

Three of the organic ligands used in this research were commercially available dyes that have been previously employed as fluorometric reagents for aluminum. These were: 2,2′-dihydroxy-1,1′-azonaphthalene-3-sulfonic acid, sodium salt (I), 2,2′-dihydroxy-1-naphthaleneazobenzene-5′-sulfonic acid, sodium salt (II), 2,4,2′-trihydroxyazobenzene-5′-sulfonic acid, sodium salt (III). The purity of these commercial dyes was found to vary between 59 and 75% as determined by means of a titanium(III) chloride titration of the azo group which was adapted from a method of Knecht and Hibbert.[3] To purify the dyes further the following procedure was used. The dyes were precipitated from aqueous solution with concentrated hydrochloric acid, washed and extracted with ethanol in a Soxhlet extractor. The product was precipitated on evaporation of the ethanol. This procedure increased the purity of I to 75%, II to 91% and III to 90%. Spectrographic analysis of the purified dyes indicated the absence of all metals other than alkali metals, salts of which constitute the chief impurities in II and III.

Since the commercial dye I was found to contain a considerable amount of organic impurity, it was decided to synthesize this compound. 1-Diazo-2-naphthol-4-sulfonic acid was treated with β-naphthol in 15% potassium hydroxide. After removal of the unreacted yellow diazo oxide by filtration, the solution was allowed to stand for 12 hours. The deep blue solution was continuously extracted with carbon tetrachloride until the extract was no longer red. The blue aqueous solution was then continuously extracted with isoamyl alcohol from which the blue basic form of the dye was obtained by filtration. This product is easily dissolved in water or alcohol.

1-(2-Hydroxybenzeneazo)-2-naphthol (IV), 2,4,2′-trihydroxyazobenzene (V) and 2,6-dihydroxy-3-(2-hydroxyphenylazo)-pyridine (VI) were prepared by standard diazotization and coupling procedures. The 2,6-dihydroxypyridine for VI was synthesized by the method of Errera.[4] 2,2′-Dihydroxyazobenzene (VII), 2,2′-dihydroxy-5,5′-dimethylazobenzene (VIII), 2,2′-dihydroxy-4,4′-dimethylazobenzene (IX) and 2,2′-dihydroxy-5,5′-dinitroazobenzene (X) were prepared by a method to be published elsewhere.

Salicylidene-*o*-aminophenol (XI) was prepared as follows. Salicylaldehyde, 124.4 g., was added to 21.8 g. of *o*-aminophenol dissolved in 1 liter of commercial absolute ethanol. The solution was refluxed for 30 minutes and cooled. The product was recrystallized from ethanol to give a 79% yield

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(1) Abstracted from the thesis of D. C. Freeman, Jr., submitted to the Graduate School of the University of Maryland, June, 1955, in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

(2) M. H. Fletcher and E. R. Warner, *Nuc. Sci. Abstr.*, **5**, 4700 (1951).

(3) E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis," Second Edition, Longmans, Green and Co., 1925.

(4) G. Errera, *Ber.*, **31**, 1241 (1898).

of fine dark red needles, m.p. 185° (lit.[5] 185°). The method of Pictet and Ankersmit[6] was used to prepare benzilidene-*o*-aminophenol (XII). Salicylidene anil (XIII) was prepared as by Hantzsch and Schab.[7]

Bis-salicylidene-*o*-phenylenediamine (XIV) was prepared by refluxing a suspension of 21.6 g. of *o*-phenylenediamine and 49.2 g. of salicylaldehyde in 1 liter of benzene for 1 hour with a Dean–Stark trap to remove the water formed. The product crystallized on cooling. This was filtered, and the residue dried and recrystallized from methanol to give an 83% yield of bright orange needles, m.p. 162.5–163.5° (lit.[8] 164°).

Bis-salicylideneëthylenediamine (XV) was synthesized as follows. A solution of 20.0 g. of 70% ethylenediamine in benzene was refluxed until all the water had been removed in a Dean–Stark trap. After addition of 49.2 g. of salicylaldehyde the solution was refluxed for 1 hour. The product crystallized on cooling and was recrystallized twice from methanol to give a 77% yield of shiny yellow plates, m.p. 124–125° (lit.[9] 125–126°).

Salicylaldehyde-azine (XVI) was prepared by adding 29.4 g. of 85% hydrazine hydrate to 1 liter of 95% ethanol containing 123 g. of salicylaldehyde and 3 drops of concentrated hydrochloric acid. After the mixture was refluxed for 30 minutes it was cooled and the product removed by filtration. Recrystallization from toluene gave an 87% yield of yellow plates, m.p. 213° (lit.[10] 213°).

The condensation product between acetylacetone and ethylenediamine (XVII) (usually known as "bis-acetylacetone ethylenediamine") was synthesized by refluxing a benzene solution of 17.2 g. of ethylenediamine and 40 g. of acetylacetone for about 6 hours with a Dean–Stark trap. Most of the benzene was then removed and the yellow solid was recrystallized from petroleum ether (60–80°) to give a 67% yield of shiny white plates, m.p. 110–111.3° (lit.[11] 111.5°).

N,N-Dimethylformamide (DMF) as a Solvent for Fluorescent Chelation.—The difficulty of preparing water-soluble chelating agents led to the selection of DMF as a suitable non-aqueous solvent. The commercial product contains some water and an impurity which has a blue fluorescence. Purification was effected by distillation at about 10 mm. pressure through a 4 foot Vigreux column under an atmosphere of nitrogen. The bulk of the distillate was water white and non-fluorescent. The solvent was easily reclaimed by the above procedure. Solutions of isobutylamine and anhydrous acetic acid, 0.5 *M*, in DMF were employed as base and acid, respectively. Methyl red was used as an indicator for volumetric standardization. A 34% DMF solution in water was also found to be a satisfactory solvent with characteristics approaching those of water.

The Screening of Compounds for Fluorescent Chelation.—The reagents were tested for the formation of fluorescent chelates in DMF with the following cations: Al^{+++},Ga^{+++}, UO_2^{++}, Th^{++++}, Li^{+}, Be^{++}, Ni^{++}, Cu^{++}, Cd^{++}, Co^{++}, Ca^{++}, Mg^{++}, Sn^{++++}, Pb^{++}, Zn^{++}, Mn^{++}, Fe^{+++}, La^{+++}, ZrO^{++}, In^{+++}, Nd^{+++}, Pr^{+++} and Ag^{+}. The general procedure was to add 1 ml. of a 2 μ mole/ml. solution of the organic compound in DMF to about 10 ml. of DMF in a 25-ml. glass-stoppered test-tube. Then 1 ml. of a 2 μ mole/ml. solution of the cation in water was added and the tube filled to the 25-ml. mark with DMF. In the case of aluminum, gallium, tin, lead and iron, the ion was in 0.2 *N* hydrochloric acid. A hydrochloric acid blank was run for each compound. Zirconium was in 5 *N* sulfuric acid and beryllium in 3 *N* hydrochloric acid. The sample solution was divided into two equal parts, one of which was treated with 0.25, 0.50 and 1.00 ml. increments of 0.5 *N* acetic acid in DMF, and the other with equivalent increments of 0.5 *N* isobutylamine in DMF. Each combination of organic compound and cation was tested for fluorescence at 7 different acidity levels. The maximum fluorescence intensity was determined from a plot of fluorometer reading *vs.* quantity of acid or base.

The procedure employed for the 34% DMF system utilized similar quantities of materials except that 5 ml. of aqueous acetate buffer was added to each tube initially, and the tube filled to the mark with 40% DMF. This results in a sample containing 34% DMF.

The Determination of Metal to Ligand Ratio.—Attempts were made to isolate the fluorescent chelates from solution at the *p*H of optimum fluorescence intensity both by extraction and precipitation. Slightly fluorescent residues were sometimes left on evaporation of fluorescing solutions, but in no case could a solid with constant stoichiometric ratio be obtained.

The method of Job[12] and the mole ratio method[13] were found to be unsatisfactory for determining the metal to ligand ratio in solution. The method of Vosburgh and Cooper[14] was employed successfully, both fluorometrically and spectrophotometrically. Both methods give the same results as indicated by the representative curves in Fig. 1. The fluorometric procedure utilizes samples prepared in the same manner as for the standard spectrophotometric procedure. The ionic strength was kept constant throughout the series of samples for one determination.

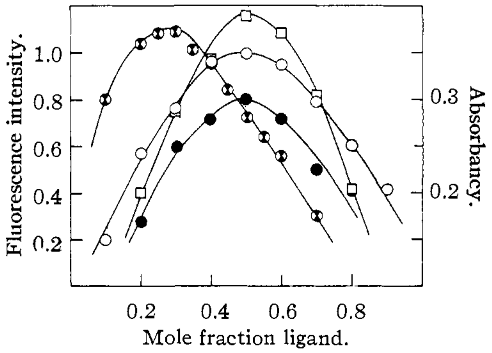

Fig. 1.—Ratio of ligand to metal by the method of Vosburgh and Cooper: ○, compound II–Al chelate in water, fluorometrically; ⊡, same, spectrophotometrically at 430 mμ; ●, same, at 310 mμ; ◐, compound XVI–Zn chelate in DMF.

A determination of metal to ligand ratio may be made kinetically in the case of chelates that have a finite time for formation. The rate of development of fluorescence of two such chelates is shown in Fig. 2. The curves indicate

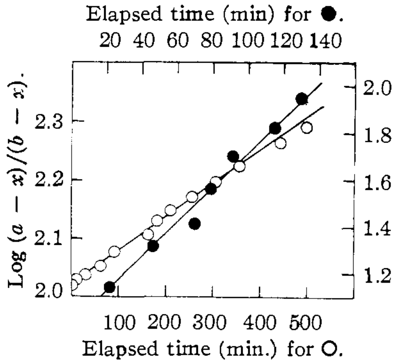

Fig. 2.—Kinetics of chelate formation as indicated by fluorescence: ○, compound III–aluminum chelate at *p*H 3.55. *C* is initial concentration of III (1.0μ mole), *a* is initial concentration of Al (100 μ moles), and *x* is concentration of chelate as indicated by fluorescence. ●, Compound VII–Gallium chelate in DMF. *d* is initial concentration of VII (2.0 μ moles), *c* is initial concentration of Ga (20.0 μ moles), and *x* is concentration of chelate as indicated by fluorescence.

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(5) E. Heagle, *Ber.*, **25**, 2755 (1892).

(6) A. Pictet and H. J. Ankersmit, *Ann.*, **266**, 140 (1891).

(7) A. Hantzsch and O. Schab, *Ber.*, **34**, 832 (1901).

(8) P. Pfeiffer and H. Pfitzner, *J. prakt. Chem.*, **2**, 145, 243 (1936).

(9) A. T. Mason, *Ber.*, **20**, 271 (1887).

(10) H. Cajar, *ibid.*, **31**, 2807 (1898).

(11) A. Combs and C. Combs, *Compt. rend.*, **108**, 1252 (1889).

(12) G. Sutra and E. Daimois, *Bull. soc. chim. belges*, **62**, 104 (1953).

(13) G. H. Ayres, *Anal. Chem.*, **25**, 1622 (1953).

(14) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

that second order kinetics are followed. This is as expected for a 1:1 complex when neither reactant is in large excess. The rate of formation of the chelates was found to be the same when the solutions were kept completely in the dark except during measurements.

Fluorescence Spectra.—The spectral distributions of the fluorescence radiation of the chelates were determined with an arrangement of the Beckman DU spectrophotometer similar to that described by McAnally.[15] At room temperature the fluorescence spectra of the chelates investigated are continuous bands of about 150 mμ width with a single maximum as seen in Fig. 3. By visual inspection through a Bunsen spectroscope a slight increase in resolution was noted at the temperature of liquid air. The lower temperature caused the fluorescent band to separate into two distinct bands with a slight bathochromic shift. No quantitative data were obtained at this temperature.

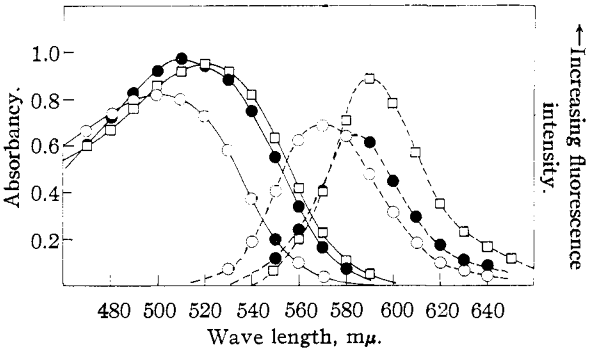

Fig. 3.—Typical fluorescence (- - - -) and absorption (——) spectra of chelates: □, compound IX–Zn; ○, compound IX–Mg; ●, compound IX–In. All chelates in basic DMF.

Discussion

Screening Results.—Table I gives a condensation of the significant screening results. In some cases the fluorescence of the organic molecule alone, particularly in weakly basic solution, caused difficulty in the screening procedure. Compounds XV, XVII and XIX fluoresce by themselves in all but a narrow range of acidity. It is believed that hydrogen bonding may cause a configuration which allows fluorescence for reasons explained in a later section.

Structure of the Chelates.—The method of Vosburgh and Cooper and the kinetic studies indicate that the azo, azomethine and salicylidenediamine chelates investigated have a 1:1 ratio of metal to ligand in accord with the work of Young and Sweet,[16] and Drew,[17] and that salicylaldehyde-azine forms a chelate with zinc in a 2:1 metal to ligand ratio.

The fact that salicylidene anil (XIII) fluoresces with aluminum in solution while benzylidene-*o*-aminophenol (XII) does not, indicates that a six-membered ring is formed in these fluorescent chelates. Holzbecher[18] has obtained the solid aluminum chelates ("salts") of these two compounds and found that the chelate of XIII fluoresces and that of XII does not.

The much weaker fluorescence of the aluminum chelate of XIII as compared to the corresponding dihydroxy compound XI indicates that two ortho hydroxy groups are much more desirable than one for fluorescent chelation.

All evidence found indicates that the structural configuration given by Drew is fundamentally correct. The work of Hendricks[19] and of Klotz[20] corroborates the proposed structure.

TABLE I

POSITIVE RESULTS OF SCREENING IN DMF

Compound	Cation	Acidity	Relative intensity
IV	Al^{+++}	Strong acid[a]	3.00
	Ga^{+++}	Weak acid[b]	1.20
	Th^{++++}	Strong acid	0.05
	In^{+++}	Neutral	.12
	Mg^{++}	Strong base[c]	.09
V	Al^{+++}	Strong acid	.16
	Ga^{+++}	Neutral	5.40
	Th^{++++}	Neutral	0.05
	Mg^{++}	Weak base[d]	.20
	Zn^{++}	Strong base	.04
	In^{+++}	Weak base	.08
VI	Al^{+++}	Weak base	.10
	Ga^{+++}	Weak acid	.07
	Th^{++++}	Neutral	.04
	Mg^{++}	Weak base	.56
	Zn^{++}	Weak base	.07
VII	Al^{+++}	Strong acid	3.20
	Ga^{+++}	Neutral	1.60
	Th^{++++}	Neutral	0.04
	Mg^{++}	Weak base	.49
	Zn^{++}	Strong base	.07
	In^{+++}	Neutral	.48
VIII	Al^{+++}	Strong acid	.14
	Ga^{+++}	Strong acid	.69
VIII	Th^{++++}	Strong base	.07
	Mg^{++}	Strong base	.64
	Zn^{++}	Strong base	.16
	In^{+++}	Strong base	.14
IX	Al^{+++}	Strong base	.10
	Ga^{+++}	Neutral	4.30
	Th^{++++}	Neutral	0.07
	Mg^{++}	Strong base	.93
	Zn^{++}	Strong base	.14
X	Ga^{+++}	Neutral	.28
XI	Al^{+++}	Neutral	69.0
	Ga^{+++}	Weak base	1.60
	Be^{++}	Weak base	23.0
	Mg^{++}	Neutral	2.00
	Zn^{++}	Strong base	2.50
	In^{+++}	Neutral	4.70
XIV[e]			
XV	Al^{+++}	Weak acid	4.60
	Mg^{++}	Weak base	58.0
	Zn^{++}	Weak base	12.0
	In^{+++}	Weak base	11.0
XVI	Ga^{+++}	Strong base	0.25
	Be^{++}	Weak base	8.40
	Zn^{++}	Neutral	1.00
XVII	Al^{+++}	Neutral	0.18

[a] Between one and three ml. of 0.5 *M* acetic acid in DMF per ml. [b] Less than one ml. of 0.5 *M* acetic acid in DMF per 25 ml. [c] Between one and three ml. of 0.5 *M* isobutylamine per 25 ml. [d] Less than one ml. of 0.5 *M* isobutylamine per 25 ml. [e] Results doubtful because of high blanks.

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(15) J. S. McAnally, *Anal. Chem.*, **26**, 1526 (1954).

(16) A. Young and T. R. Sweet, *ibid.*, **27**, 418 (1955).

(17) H. D. K. Drew, *et al.*, *J. Chem. Soc.*, 292 (1938); 823 (1939); 603, 608, 1064 (1940).

(18) Zavis Holzbecher, *Chem. Listy*, **47**, 1023 (1953), *C. A.*, **49**, 947 (1955).

(19) S. B. Hendricks, *et al.*, THIS JOURNAL, **58**, 1991 (1936).

(20) I. M. Klotz, *et al.*, *ibid.*, **76**, 5136 (1954).

It may be seen from the models of these compounds that there is a strong similarity between the "chelating centers" of all of these molecules. There seems to be a basic structure involved in the formation of fluorescent chelates of this type. This led to the testing of the aliphatic compound XVII for fluorescent chelation to see if aromaticity was a necessary part of this basic structure. The weak fluorescence of this compound with aluminum indicates that aromaticity is desirable but not absolutely necessary.

All of the compounds investigated form several other chelates besides those which fluoresce. There is a marked difference between the fluorescent and the non-fluorescent chelates. Many of the non-fluorescent chelates with the transition metals have been investigated[14,21] and these compounds are almost invariably assumed to be covalently bonded.

The table of screening data, of the cations tested, shows that those which form fluorescent chelates are aluminum, beryllium, gallium, indium, magnesium and zinc. These metals do not generally form chelates with small instability constants.

Further evidence that the fluorescent chelates are ionic is seen in the spectrophotometric curves, of which Fig. 4 is typical. Except for the usual bathochromic shift and the intensification of the longest wave length absorption band, the curves for the compound alone and the chelate are quite similar. This is indicative of an ionic bond type chelate.[22]

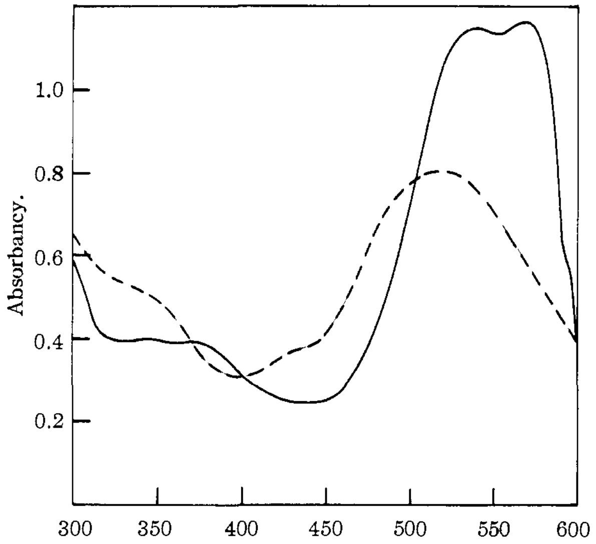

Fig. 4.—Typical absorption curve: - - - -, compound I (10^{-4} moles/l.), *p*H 4.63; ——, compound I-Al chelate, same conditions; 5 mμ readings.

It has been established that ionic forces for chelation depend on the charge and radius of the cation, while covalent forces depend on the relative tendencies for various metals to form covalent bonds.[23] A definite correlation between the ratio of charge squared to radius of the cations and the intensity of fluorescence of the chelate was found, as shown in Fig. 5. If the fluorescence intensity may be taken as a measure of the stability of the chelate then ionic bonding is clearly indicated. No such correlation could be found between fluorescence intensity and known covalent bonding tendencies of the metals.

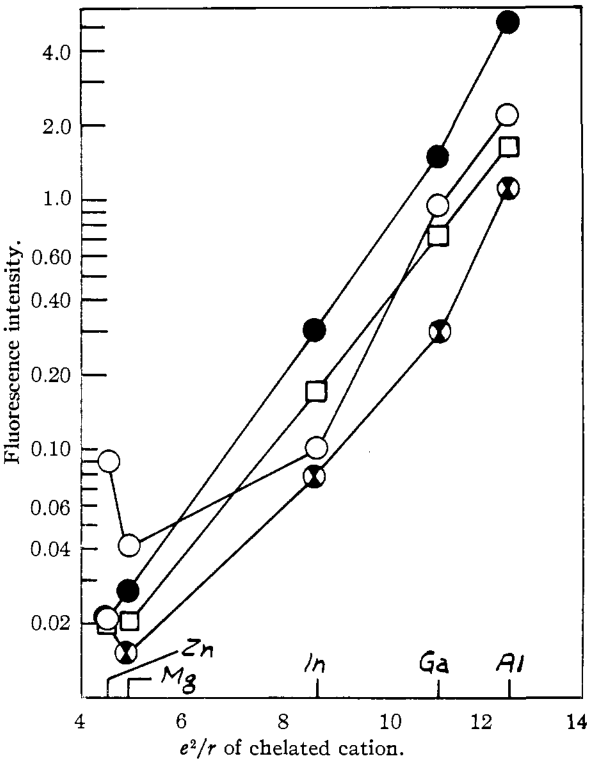

Fig. 5.—Dependence of chelate stability to e^2/r, where e = charge and r = radius of ion, as indicated by fluorescence intensity: ● is compound V, ○ is compound VIII, □ is compound IV, and ⊗ is compound VII; all chelates in 34% DMF–Water.

Effect of Structure on Fluorescence.—Spectrofluorescence curves for these chelates show that the intensity of fluorescence which may be obtained by irradiation at a given wave length is directly proportional to the absorbancy of the chelate at that wave length. No correlation could be found between the wave length of the fluorescence band maximum of a chelate and any property of the different metals forming chelates with the same compound. These wave lengths, with the wave lengths of the longest absorption bands and the energy difference between the two, are tabulated in Table II. There is a definite relationship between the longest absorption band and the fluorescence band. Although the energy differences between the two are fairly constant the variations in those differences are outside the experimental error.

There seems to be some effect of substituent groups on the wave length of the fluorescence. Those groups which cause the more pronounced resonance effects produce the major change in wave length; no other correlation was found in these experiments. The intensity of the fluorescence appears to follow the order expected from a consideration of the electron donating ability of the groups. This may be seen on Fig. 5; however, the

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(21) J. C. Bailar, THIS JOURNAL, **74**, 6018 (1952).

(22) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, section 2.5.

(23) Ref. 22, p. 183.

TABLE II

ABSORPTION AND FLUORESCENCE BAND MAXIMA IN DMF

Compound	Cation	Acidity	Longest as. band, mμ	Fluorescence band, mμ	Energy difference, kcal./mole
VII	Ga^{+++}	Neutral	492	591	9.8
	Al^{+++}	Acid	430	577	16.9
	Mg^{++}	Basic	505	578	7.1
	Zn^{++}	Basic	519	594	6.9
	In^{+++}	Neutral	435[a]	580	16.4
IV	Ga^{+++}	Acid	521	597	7.0
V	Ga^{+++}	Neutral	487	567	8.2
VI	Ga^{+++}	Neutral	435[a]	547	13.4
X	Ga^{+++}	Neutral	501	565	6.4
VIII	Ga^{+++}	Acid	520	596	7.0
	Al^{+++}	Acid	455[a]	578	13.3
	Mg^{++}	Basic	485[a]	589	10.4
	Zn^{++}	Basic	535	615	6.9
	In^{+++}	Basic	536	613	6.7
IX	Ga^{+++}	Neutral	495	578	8.3
	Al^{+++}	Basic	520	589	6.4
	Zn^{++}	Basic	520	588	6.3
	Mg^{++}	Basic	500	580	7.9
	In^{+++}	Basic	510	583	7.0

[a] The longest wave length bands may have been masked by larger bands with maxima at wave lengths given.

number of compounds is insufficient to rule out coincidence.

The *p*H values for maximum fluorescence of the azo chelates are only approximate because of the lack of sharp maxima in the curves of fluorescence intensity *vs. p*H. The precipitation *p*H values for hydrous oxides as given by Moeller[24] are plotted against the *p*H at which maximum fluorescence is obtained in Fig. 6. The upper limit of *p*H appears to be established by the chelating agent. This may well be the reason why the fluorescence intensities of the magnesium and zinc chelates are uniformly low in Fig. 5. The fluorescence intensity would be expected to be independent of the *p*H so long as the *p*H can be adjusted to give the optimum charge effects for chelation. The maximum *p*H as dictated by the chelating agent might be too low to produce these optimum effects for magnesium and zinc chelation.

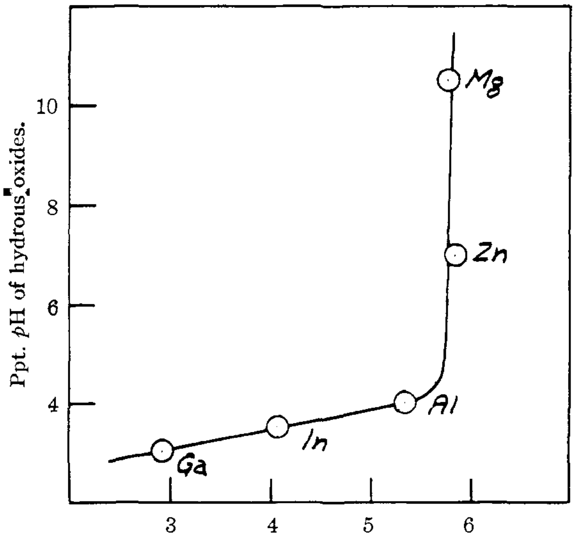

Fig. 6.—Correlation between precipitation *p*H of the metal and the *p*H value for greatest stability of the chelate as evidenced by maximum fluorescence. Each *p*H value for maximum fluorescence is the average of the five values obtained for chelates of each signified metal with compounds IV, V, VII, VIII and IX.

An explanation as to why the chelates fluoresce and the chelating agents do not under the same conditions is of fundamental interest. The organic compounds under investigation all have in common a single axis, for example, the azo group, about which two major portions of the molecule can rotate to some degree. This is an ideal situation for internal conversion.[25] If the rotation can in some way be stopped, there will be a very low probability of the molecule reaching the particular configuration that allows internal conversion; and fluorescence may occur. When the non-chelated organic molecules were dissolved in acetamide and the solution was solidified and cooled with liquid air a fluorescence was produced. Under these conditions it can be assumed that the rotation of the molecule is decreased. It is logical that the favored configuration on ceasing of rotation would be the planar one in which stabilizing resonance can occur. The characteristics of the fluorescence of the "frozen" molecules are identical with those of the same molecules in the chelated condition; and so it is postulated that chelation forces the molecules into planar configuration and thus prevents internal conversion and permits fluorescence.

Covalent bonding appears to allow the ready transfer of excitation energy from the organic molecule to the metal atom, and ionic bonds prevent this energy transfer. It is therefore possible that those metals which are covalently bound by the compounds under investigation serve as energy dissipators and pass the excitation energy absorbed by the organic molecule into the solution. The fact that the transition element cations which form covalent chelates are well known for quenching by collision indicates that the transfer of energy from the cation to the solution is not difficult.

Acknowledgments.—Financial support of this research by Arthur D. Little, Inc., is gratefully acknowledged.

COLLEGE PARK, MD.

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(24) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 502.

(25) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949.