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

An Infrared Study of the Metal Chelates of Some Imidazole Derivatives[1]

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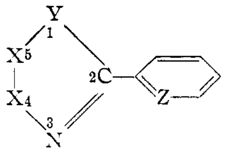
RECEIVED JUNE 16, 1955

Infrared absorption curves have been obtained in the 2–15 μ region for a series of metal chelates of 2-(2-pyridyl)- and 2-(*o*-hydroxyphenyl)-derivatives of benzimidazole, imidazoline, benzoxazole and benzothiazole. Use was made of the potassium bromide pressed pellet technique for the preparation of samples. Particular attention has been focussed on the 3 μ region in order to observe the effects of coördination on the N–H stretching frequency. Coördination of the reagent with a metal ion decreases the N–H stretching frequency. This is explained in terms of resonance structures. Evidence is given for an intramolecular chelate structure in 2-(*o*-hydroxyphenyl)-benzimidazole. 2-(*o*-Hydroxyphenyl)-benzoxazole and its chelates have an absorption band at 8.0 μ (1250 kayser) which undergoes a regular shift, paralleling the usual stability order of the metals. The copper(II) chelate is at the highest frequency.

Introduction

This paper deals with an infrared spectroscopic study of a series of related heterocyclic compounds and their metal chelates which was undertaken to investigate the effects of metal bonding upon the characteristic absorption frequencies of the compounds. The compounds included in this work may all be represented by the skeletal structure



where X–X is either CH_2–CH_2 or C_6H_4; Y is either N–H, O, or S; and Z is either N or C–OH.

In those compounds where Z was C–OH, chelation was accompanied by a neutralization of charge while for those in which Z was N, chelation occurred between the two pyridyl nitrogen atoms and the metal with no charge neutralization.

The potassium bromide pressed disk technique[2,3] has been used to obtain the spectra of these solid metal complexes.

Considerable interest centered around the 3 μ region of the spectra (N–H stretching vibration region) of those compounds containing an N–H group since a potentiometric study of some substituted imidazole complexes[4] had produced evidence of the dependence of the acidity of the N–H grouping upon the metal ion present. Depending on the nature of the nitrogen-to-metal linkage, one might expect some type of electronic interaction through the imidazole ring system that will in some way affect the strength of the N–H bond.

Experimental

Materials.—2-(*o*-Hydroxyphenyl)-benzoxazole was prepared by the method outlined by Siegfried and Moser.[5]

2-(*o*-Hydroxyphenyl)-benzimidazole was prepared by the procedure outlined in a paper by Walter and Freiser.[6]

2-(2-Pyridyl)-benzimidazole was prepared according to the procedure given by Leko and Vlajinats.[7]

2-(2-Pyridyl)-imidazoline was prepared by the procedure outlined in a paper by Walter and Freiser.[8]

The procedure for the preparation of 2-(2-pyridyl)-benzoxazole was analogous to that followed in the preparation of 2-(2-pyridyl)-benzimidazole.

One mole of α-picolinic acid and one mole of *o*-aminophenol were heated together for three hours in a distilling flask immersed in an oil-bath at a temperature of 160–170°. The product was then distilled at atmospheric pressure. The product was recrystallized three times from an alcohol–water mixture to give the 2-(2-pyridyl)-benzimidazole which melted at 104–106°. *Anal.* Calcd. for $C_{12}H_8N_2O$: N, 14.25. Found: N, 14.40.

The preparation of 2-(*o*-hydroxyphenyl)-imidazoline is given in a thesis by W. D. Johnston.[9]

Equimolar amounts of salicylamide and ethylenediamine were heated together in a distilling flask at 140–150° for two hours after which the temperature was raised to 175–185° and the heating continued for another two hours. Both water and ammonia were evolved. The mixture was then distilled at approximately 330°. After decolorization with charcoal and recrystallization from an alcohol–water mixture, the product melted at 200–203°.

Solutions of each of the aforementioned organic reagents having a concentration of 20 mg. per ml. were prepared in 95% ethanol and used in aliquots as needed to form the various metallic complexes.

Reagent grade nitrates of copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II), lead(II), manganese(II), magnesium(II) and iron(II) were used to prepare solutions which contained 50 mg. of metal per ml. for use in preparing the various metallic chelates.

Ten per cent. solutions of reagent grade sodium perchlorate, potassium bromide and potassium iodide were used to precipitate the metallic complexes of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline.

Potassium bromide powder for making disks was prepared as follows.

Reagent grade crystalline potassium bromide was ground in a motor-driven mortar for several hours. The resultant powder was dried at 130° for three days and then kept in a desiccator until used.

Apparatus.—A one inch (i.d.) metallurgical mold assembly obtained from Buehler Co., Chicago, Illinois, was used in conjunction with a Thiele testing apparatus with a capacity of 60,000 p.s.i. to press the potassium bromide disks.

A Model 12-C Perkin–Elmer Recording Infrared Spectrometer equipped with sodium chloride optics was used for all infrared measurements. The frequencies given are accurate to at least ±10 kayser (±0.01 μ) in the 3 μ region.

Preparation of Metal Chelates.—A number of qualitative observations were made using the various reagents and the metal ions mentioned under materials. The *p*H was varied to obtain the optimum conditions for precipitation. Also, in the cases of the reagents forming charged, soluble complexes with the metals, several anions, *e.g.*, perchlorate, chloride, iodide and bromide, were tried in an effort to precipitate the compounds so as to obtain solid chelates for the infrared investigation.

The following procedures represent the optimum conditions found for the preparation of the chelates used in this study.

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[1] Presented in part at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1955.

[2] M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

[3] U. Schiedt and H. Reinwein, *Z. Naturforsch.*, **7b**, 270 (1950).

[4] T. R. Harkins and H. Freiser, THIS JOURNAL, in press.

[5] S. Siegfried and M. Moser, *Ber.*, **55**, 1089 (1922).

[6] J. L. Walter and H. Freiser, *Anal. Chem.*, **25**, 127 (1953).

[7] A. Leko and G. Vlajinats. *Bull. soc. chim. roy. Yougoslav.*, **1**, 3 (1930).

[8] J. L. Walter and H. Freiser, *Anal. Chem.*, **26**, 217 (1954).

[9] W. D. Johnston, Ph.D. Thesis, University of Pittsburgh, 1953.

Chelates of 2-(*o*-Hydroxyphenyl)-benzoxazole.—One milliliter of each of the metal ions to be precipitated as a chelate was pipetted into small beakers. Ten milliliters of distilled water was then added to each. An aliquot of the reagent solution containing the amount necessary to precipitate each of the metals was then added to each of the samples. The *p*H of each solution was adjusted to the optimum *p*H as determined from the qualitative reactions. For Cu the optimum *p*H was 4, for Cd 10, and for Ni, Co, etc., a value of 7. The precipitates were filtered and washed several times with 50% ethanol-water solution. The precipitates were then transferred to small sample vials and dried at 130° for several hours. This was the only purification procedure given these chelates. Since they were so insoluble, no solvent could be found to offer any suitable means of recrystallization.

Chelates of 2-(*o*-Hydroxyphenyl)-benzimidazole.—Essentially the same procedure as outlined above for the preparation of the chelates of 2-(*o*-hydroxyphenyl)-benzoxazole was used to obtain the chelates of 2-(*o*-hydroxyphenyl)-benzimidazole. However, from the qualitative tests made with this reagent, it was discovered that only the chelates of copper(II), cobalt(II) and zinc(II) could be prepared readily. The copper(II) chelate was precipitated in a neutral solution, while the cobalt(II) and zinc(II) chelates were precipitated in a slightly basic solution (*p*H 8).

Chelates of 2-(*o*-Hydroxyphenyl)-imidazoline.—The chelates of this reagent were also prepared in the same manner as the above-mentioned chelates. The qualitative tests indicated that it was possible to obtain as solids only the copper(II), nickel(II), cobalt(II) and zinc(II) chelates. The copper(II) chelate was precipitated from a neutral solution, and the cobalt(II), nickel(II) and zinc(II) chelates were precipitated from a slightly basic solution.

Chelates of 2-(2-Pyridyl)-benzimidazole.—From qualitative tests with metals and this reagent it was found that all of the metals formed soluble, charged complexes with the reagent much in the same manner as 2,2′-bipyridine and *o*-phenanthroline. Thus, a suitable anion that would give a precipitate had to be sought. From the group of anions tried, it was found that the perchlorate, bromide and iodide ions gave precipitates with copper(II), cobalt(II), nickel(II) and zinc(II) complexes.

One milliliter each of the metal ion solutions of copper(II), nickel(II), cobalt(II) and zinc(II) was pipetted into small beakers. Ten milliliters of distilled water was added. An aliquot of the reagent solution containing the amount necessary to complex the metal was added. The *p*H was adjusted to about six. Then about five milliliters of the prepared sodium perchlorate solution was added to each sample. The perchlorates of the complexes immediately separated from solution. The precipitates were filtered and recrystallized from hot water. The recrystallized complex was filtered and washed several times with cold 30% alcohol-water solution. These precipitates were dried at 130°.

In order to prepare the iodides and bromides of the metal complexes of 2-(2-pyridyl)-benzimidazole, exactly the same procedure as was outlined for the precipitation of the perchlorates was utilized except that the precipitating anion was either the prepared iodide or bromide solution in place of the perchlorate solution.

Chelates of 2-(2-Pyridyl)-imidazoline.—Exactly the same procedure used to prepare the perchlorates of the metal complexes of 2-(2-pyridyl)-benzimidazole was employed to prepare the chelates of 2-(2-pyridyl)-imidazoline. For this study the 2-(2-pyridyl)-imidazoline iodides of copper(II), nickel(II), cobalt(II) and zinc(II) were prepared as well as the imidazoline bromides of the same metals. The imidazoline complexes are much more soluble in an alcoholic-water solution than are the 2-(2-pyridyl)-benzimidazole complexes, and so care must be exercised in the washing of the chelates. The precipitates are dried at 130°.

The results of microanalyses are given in Table I for those compounds having the expected stoichiometry.

Preparation of Potassium Bromide Sample Disks.—Since the chelates as a whole were insoluble in organic solvents, it was necessary to employ a method for handling solids. The potassium bromide pellet technique was chosen.[2,3] This technique rather than the oil mull technique was used as paraffin oil has a strong absorption band in the 3 μ region, which would be undesirable in this study.

For the qualitative type work undertaken in this investigation, it was found that the following method for the preparation of the potassium bromide sample disks was most adequate.

A sample of from 5–7 mg. of the compound to be studied, along with 800 mg. of the prepared potassium bromide powder, was thoroughly mixed and ground together in an agate mortar. This grinding took about three minutes per sample. The thoroughly mixed sample–potassium bromide preparation was then transferred into the mold and distributed evenly. A pressure of 24,000 p.s.i. was applied to the mold for ten minutes. Although entirely transparent disks were not produced by this method, disks with a sufficiently large enough transparent area for study were obtained. In so far as this study could reveal, the prepared discs can be stored in a desiccator for an indefinite period of time before an infrared curve is obtained for the sample. Several curves run over a period of several weeks on the same disk showed no marked differences in any of the absorption peaks.

Discussion

3 μ Absorption Bands (Table I).—2-(2-Pyridyl)-benzimidazole has a broad absorption band in the 3 μ region (3040 kayser), which is doubtless due to the N–H stretching vibration. A spectrum of 2-(2-pyridyl)-benzoxazole, an identical molecule except that an oxygen atom replaces the N–H group, does not show an absorption band in this region. The broadness and tapering off of the absorption band in the direction of lower frequencies is indicative of a strong hydrogen bonding effect operating on the N–H bond. It is not surprising to find this effect since benzimidazoles and imidazoles possessing a free imino hydrogen are known to be capable of associating.[10]

The association is predominantly intermolecular in nature rather than intramolecular since a dilute solution of the compound in chloroform has a very sharp peak at a much higher frequency (3435 kayser).

Sutherland[11] has suggested that hydrogen bonding should be considered only for bands in which $\Delta\bar{\nu}/\bar{\nu} > 3\%$ since a change in state will also result in a change in frequency. From the data of Table I one can calculate band differences of 12 and 6% for 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline, respectively.

Depending on the packing of the molecules in the solid state, any one or all of the three nitrogens in the molecule could enter into hydrogen bonding.

The solid metal chelates of 2-(2-pyridyl)-benzimidazole have their N–H absorption peaks around 3000 kayser. Either there still is considerable intermolecular hydrogen bonding in the solid because of the close packing of the molecules, or else because of chelation there is a pronounced shift of the free N–H absorption to lower frequencies. Since the two basic pyridine nitrogens of the reagent are being utilized for complex formation, one would expect a lesser degree of hydrogen bonding to occur between molecules of the chelates than between molecules of the reagent itself. In no event is the N–H absorption frequency of the chelate at a higher frequency than the band observed for the solid reagent. One might possibly infer then that coordination with a metal results in a decrease of the N–H stretching frequency.

The same effect is noted for the chelates of 2-(2-pyridyl)-imidazoline.

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(10) K. Hofmann, "Imidazole and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1953.

(11) G. B. B. M. Sutherland, *Trans. Faraday Soc.*. **36**, 889 (1940).

TABLE I

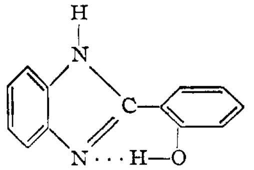
3μ ABSORPTION FREQUENCIES AND ANALYSES

		Stretching frequencies (kayser)[c]			Nitrogen, %	
Compound	Formula	N–H	CH_2	O–H	Calcd.	Found
2-(2-Pyridyl)-benzimidazole	$C_{12}H_9N_3$	3040	..	..	13.69	13.85
		3435[a]				
Chelates	$Ni(C_{12}H_9N_3)_3I_2$	3030			14.04	13.78
	$Co(C_{12}H_9N_3)_3I_2$	3010			14.03	13.85
	$Zn(C_{12}H_9N_3)_2I_2$	3005			11.84	12.18
	$Cu(C_{12}H_9N_3)_2Br_2$	3040			13.69	13.85
	$Ni(C_{12}H_9N_3)_3Br_2$	2995			15.68	15.45
	$Co(C_{12}H_9N_3)_3Br_2$	3005			15.67	15.52
	$Ni(C_{12}H_9N_3)_3(ClO_4)_2$	3005			14.95	14.51
	$Co(C_{12}H_9N_3)_3(ClO_4)_2$	3020			14.95	14.71
2-(2-Pyridyl)-imidazoline	$C_8H_9N_3$	3215	2900	..	28.55	28.32
		3415[b]	2855[b]			
			2930[b]			
Chelates	$Ni(C_8H_9N_3)_3I_2$	3175	2900		16.72	16.41
	$Co(C_8H_9N_3)_3I_2$	3175	2900		16.71	16.72
	$Zn(C_8H_9N_3)_2Br_2$	3085	2900		16.18	16.27
		3210				
2-(*o*-Hydroxyphenyl)-benzimidazole	$C_{13}H_{10}N_2O$	3155	..	2530	13.32	13.62
Chelates	$Cu(C_{13}H_9N_2O)_2$	2985	..	..	11.63	11.34
	$Co(C_{13}H_9N_2O)_2$	3105			11.74	12.17
	$Zn(C_{13}H_9N_2O)_2$	2995			11.58	12.01
2(-(*o*-Hydroxyphenyl)-imidazoline	$C_9H_{10}N_2O$	2995	2845	2655	17.28	17.23
Chelates	$Cu(C_9H_9N_2O)_2$	3065	2845	..	14.52	14.79
	$Ni(C_9H_9N_2O)_2$	3080	2845		14.71	15.03
	$Co(C_9H_9N_2O)_2$	3155	2845		14.70	14.82
	$Zn(C_9H_9N_2O)_2$	3080	2845		14.45	13.81
2-(*o*-Hydroxyphenyl)-benzoxazole	$C_{13}H_9NO_2$	..	..	..	5.25	5.21
Chelates	$Cu(C_{13}H_8NO_2)_2$				5.79	6.24
	$Ni(C_{13}H_8NO_2)_2$				5.85	6.37
	$Co(C_{13}H_8NO_2)_2$				5.85	6.26
	$Zn(C_{13}H_8NO_2)_2$				5.77	6.14
	$Pb(C_{13}H_8NO_2)_2$				4.46	4.93
	$Mg(C_{13}H_8NO_2)_2$				6.30	6.60
	$Cd(C_{13}H_8NO_2)_2$				5.26	5.21
	$Mn(C_{13}H_8NO_2)_3$				5.89	6.28

[a] Dilute solution in $CHCl_3$. [b] Dilute solution in CCl_4. [c] Kayser = $cm.^{-1}$.

Considering now the reagents having an *o*-hydroxyphenyl-group as the substituent in the 2-position, it was found that 2-(*o*-hydroxyphenyl)-benzimidazole has a broad absorption band centered at about 2530 kayser, which would probably be due to the O–H stretching vibration. The corresponding 2-(2-pyridyl)-benzimidazole, which has no O–H bond, does not show this absorption.

Since the O–H absorption band of this reagent is at such a low frequency, this would be evidence for the existence of a "chelated" O–H bond in the reagent itself. Hunter and Marriott[12] have postulated this structure from a consideration of its lack of molecular association. The differences in the ultraviolet absorption spectra of the *o*- and *m*- and *p*-hydroxyphenyl derivatives of benzimidazole have also been shown.[13]



There is a distinct difference in the 3 μ region between the curve of the reagent and those of the chelates. The chelates, for example, no longer have the broad absorption band at 2530 kayser since the O–H bond has been broken in the formation of the metal complex. Here also the chelates exhibit a lower N–H stretching frequency than the reagent itself.

2-(*o*-Hydroxyphenyl)-imidazoline behaves very similarly to the corresponding benzimidazole. Although in this instance the N–H stretching vibrations of the chelates are at a higher frequency than that of the reagent, they are still at a much lower frequency than one would expect for a "free" N–H stretching vibration.

Interpretation of N–H Frequency Shift.—Flett[14] has examined a series of *para*-substituted anilines and has observed a regular variation in both the symmetric and anti-symmetric N–H stretching frequencies. Those derivatives having a strong electron withdrawing group in the *para*-position have their N–H vibrations at a higher frequency than those with a weak electron withdrawing group in the same position. This can be related to the

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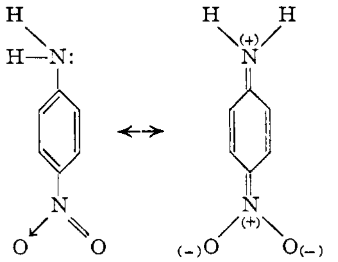
[12] L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 777 (1941).

[13] Chr. Wiegand and E. Merkel, *Ann.*, **557**, 242 (1947).

[14] M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

double bond character of the carbon to nitrogen linkage and is a measure of the relative contribution of resonance structure (2) to the ground state of the molecule.

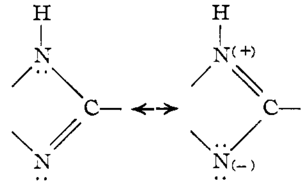


(1) (2)

In contrast to this, Quagliano, Curran, *et al.*,[15,16] have found from an examination of a large number of compounds containing ammonia molecules or NH_2 groups that the formation of a nitrogen to metal bond results in a decrease in the N–H stretching frequency. Their shifts in the absorption peaks attributed to N–H stretching vibrations increase with increasing charge on the metal ion and with increasing covalent character of the nitrogen to metal bond.

For the data presented at this time, it is quite probable that coördination of these imidazole derivatives with a metal ion also results in a decrease of the N–H stretching frequency, which would also be contrary to the observations on the *para*-substituted anilines.

In an analogous manner to *p*-nitroaniline, one can write the following resonance structures for the imidazole derivatives.



(3) (4)

At first glance these appear to be comparable to structures (1) and (2) in having a resonance hybrid containing the group $\gt N^{(+)}H$. There is a difference, however.

Going from structure (1) to (2) involves a change in hybridization of the amine nitrogen (*i.e.*, going from p to sp^2 type bonds). Increasing the amount of s character in the N–H bond would effectively increase the N–H stretching frequency. A strong electron-withdrawing group in the *para*-position would tend to increase the contribution of structure (2) to the ground state of the molecule. The influence of bond hybridization on stretching frequency has been exemplified for the C–H stretching vibrations of ethane, ethylene and acetylene (sp^3, sp^2 and sp bonding, respectively).[17] The C–H stretching frequency is the highest for acetylene.

To go from structure (3) to (4), however, does not require a change in bond hybridization. Here one is concerned with a pyrrole type nitrogen which has essentially sp^2 trigonal bonds, with its lone pair of electrons perpendicular to the plane of the molecule and capable of delocalization. Coördinating the pyridine nitrogen to a metal will increase the contribution of structure (4) to the ground state of the molecule. This will decrease the N–H stretching frequency because of the formal positive charge on the pyrrole nitrogen. This same effect is present in the case of *p*-nitroaniline but is overshadowed by the change in hybridization.

Coördination of the ammonia molecule or an NH_2 group directly to a metal would also place a formal positive charge on the nitrogen and thereby cause the N–H stretching vibration to shift to lower frequencies as has been observed.[15,16]

For the compounds reported on here the exact magnitudes of the shifts are not readily discernible because of the tendency of the molecules to associate with one another.

An attempt to correlate the frequency of the N–H stretching vibration with the relative stabilities of the metal–reagent complexes does not meet with much success, especially when one tries to compare the metal series of one reagent with another. Structural differences arising from the variance in coördination numbers of these metals and the packing of the molecules in the solid state might possibly explain these minor variations. Analysis of these compounds in solution would probably clarify the latter difficulty, but the relative insolubility of the compounds in suitable solvents provides an experimental obstacle.

8 μ Region.—Although the spectra of any particular reagent and its chelates were generally similar over the range of about 2–15 μ, one band centering around 1250 kaiser was found to undergo a regular shift from one metal chelate to another. The most noticeable shift occurred for the chelates of 2-(*o*-hydroxyphenyl)-benzoxazole, and the exact positions of this band are as follows

2-(*o*-Hydroxyphenyl)-benzoxazole		1246 kaiser
Chelates................	Cu(II)	1261 kaiser
	Ni(II)	1252
	Co(II)	1250
	Zn(II)	1249
	Pb(II)	1236
	Mg(II)	1253
	Cd(II)	1248
	Mn(II)	1248

Mellor and Maley[18] have pointed out that the stability of complexes of divalent ions follows the order

$$\mathrm{Cu} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Co} > \mathrm{Zn} > \mathrm{Cd} > \mathrm{Mn} > \mathrm{Mg}$$

irrespective of the nature of the ligands involved. Charles and Freiser[19] have established the probable relative stability order of various divalent metal complexes of 2-(*o*-hydroxyphenyl)-benzoxazole and found it to be essentially the same as the Mellor–Maley series with the exception of an apparent reversal of order in the case of nickel and cobalt and

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[15] J. V. Quagliano, G. V. Svatos and Bro. C. Curran, *Anal. Chem.*, **26**, 429 (1954).

[16] Bro. C. Curran, D. N. Sen, S. Mizushima and J. V. Quagliano, THIS JOURNAL, **76**, 429 (1954).

[17] A. D. Walsh, *J. Chem. Soc.*, 398 (1948).

[18] D. P. Mellor and L. E. Maley, *Nature*, **159**, 379 (1947); **161**, 436 (1948).

[19] R. G. Charles and H. Freiser, *Anal. Chim. Acta*, **11**, 1 (1954).

with lead placed somewhere between zinc and magnesium.

The relative order obtained from a consideration of frequency shifts is

$$Cu > Mg > Ni > Co > Zn, Cd, Mn > Pb$$

The order is practically the same as the usual stability order of divalent metal ions[18] and also that found by Charles and Freiser.[19] The most notable difference is the variance in the position of magnesium. The anomalous magnitude of the frequency shift in the magnesium chelate might be related to the relatively low mass of magnesium.

The same type of shift for this peak has also been observed for the chelates of 2-(*o*-hydroxyphenyl)-derivatives of benzimidazole, imidazoline, benzothiazole and benzothiazoline.

In each series the copper chelate, which is the most stable of the reagent–metal complexes, has its 1250 kayser absorption peak at the highest frequency, while the zinc chelate, which is generally less stable than that of the nickel or cobalt, is at the lowest frequency. This behavior is very similar to that observed for the chelates of 8-hydroxyquinoline and derivatives.[20]

Acknowledgment.—The authors are indebted to Professor Mary E. Warga of the Physics Department for the use of the infrared spectrometer and to Professor Alfred Berger of the Engineering Department for the use of the press. They gratefully acknowledge the financial assistance of the U. S. Public Health Service.

(20) R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard and W. D. Johnston, *Spectrochimica acta*, **8**, in press (1956).

PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Dipole Moments of Metal Chelate Compounds. I. Analog of Bisacetylacetone-ethylenediimine[1]

BY PAUL J. McCARTHY AND ARTHUR E. MARTELL

RECEIVED JANUARY 31, 1955

Dielectric constants of benzene solutions of bisacetylacetone-ethylenediimine, bisacetylacetonepropylenediimine, bistrifluoroacetylacetone-ethylenediimine, bisbenzoylacetone-ethylenediimine, bisbenzoylacetonepropylenediimine and bisbenzoylacetonetrimethylenediimine have been measured, and the values of the corresponding molar polarizations and dipole moments are reported. The magnitudes of the dipole moments are interpreted in terms of rotation of two hydrogen-bonded chelate rings about the alkylene bridge.

This is the first of a series of research reports on the dipole moments of chelating agents and metal chelate compounds. The analogs of bisacetylacetone-ethylenediimine were chosen as promising reagents with which to begin this program because the structures involved are relatively simple, and because many of the corresponding metal chelate compounds are soluble in benzene. The tetradentate ligands synthesized for this investigation are summarized in formula I. The names of the compounds, the substituents R, R′ and R″, and the values of *n* are given in Table I.

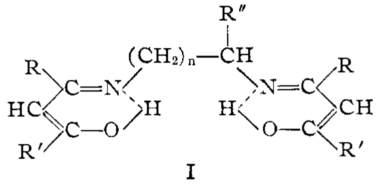

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TABLE I

LIGAND STRUCTURES

n	R	R′	R″	Name of ligand
1	CH_3	CH_3	H	Bisacetylacetone-ethylenediimine
1	CH_3	CH_3	CH_3	Bisacetylacetonepropylenediimine
1	CH_3	CF_3	H	Bistrifluoroacetylacetone-ethylenediimine
1	C_6H_5	CH_3	H	Bisbenzoylacetone-ethylenediimine
1	C_6H_5	CH_3	CH_3	Bisbenzoylacetonepropylenediimine
2	C_6H_5	CH_3	H	Bisbenzoylacetonetrimethylenediimine

Of these substances, only the parent compound, bisacetylacetone-ethylenediimine has been previously reported.[2] The trifluoro derivative also has been prepared by Martell, Belford and Calvin.[3]

Experimental

Apparatus.—A sensitive heterodyne-beat apparatus was set up with a variable-frequency oscillator and a crystal-controlled, fixed-frequency oscillator, both of which were fed into a stable receiver with a loudspeaker as detector. Since the beats near the null point were clearly audible, good precision (1 part in 10^6) was obtained in all capacitance measurements. The fixed-frequency oscillator was constructed according to the circuit of the Blily Model 1C oscillator, with modification which allowed the use of the oscillator at 100 kc. per second as well as the normal operating frequencies of 500 and 1000 kc. per second. The receiver was a National HRO "60" model. The variable-frequency oscillator was a frequency meter, BC-221-T, made by the Zenith Radio Corporation for the Army Signal Corps. A General Radio Type 722-D 1100 $\mu\mu$f. precision condenser was connected to the frequency meter in parallel with the experimental dielectric constant cell. The precision condenser was internally calibrated at 10 $\mu\mu$f. intervals in a manner similar to that suggested by Smyth.[4] The corrections were plotted against readings of the condenser and were used to correct all subsequent capacitance measurements.

The glass dielectric constant cell contained three rigidly-mounted platinum cylinders, spaced 0.07 cm. apart. The inner and outer cylinders were connected together and

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(1) (a) Abstracted from a dissertation submitted by Paul J. McCarthy, to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This work was supported by a grant from Research Corporation and by the Office of Ordnance Research under Contract No. DA19-020-ORD-3243.

(2) A. Combes and C. Combes, *Compt. rend.*, **108**, 1252 (1889).

(3) A. E. Martell, L. Belford and M. Calvin, unpublished results.

(4) C. P. Smyth, "Determination of Dipole Moments," in "Physical Methods of Organic Chemistry," A. Weissberger, Editor, Vol. I, Part II, Interscience Publishers, New York, N. Y., 1945, pp. 1005 ff.