tertiary nitrogen atoms. A precedent for such structures is found in the compounds of platinum(II) and palladium(II).[24] There appear to be no known bidentate derivatives of PDTA or EDTA for which other structures have so much as been proposed. It is not unlikely that all four carboxyl groups invariably are replaced before the nitrogen atoms for both PDTA and EDTA.

A point of difference in the reactions of Co(PDTA)$^-$ and of Co(EDTA)$^-$ requires emphasis. The former (Co(PDTA)$^-$) exhibits stereospecificity of the sort usually expected, that derived from steric repulsion. In contrast, the stereospecificity of the reaction of Co(EDTA)$^-$ with en derives from the low symmetry of the complex and the odd number of kinetically equivalent paths. In a sense, the latter is derived statistically. The contention that the PDTA case truly involves steric effects is supported further by the fact that reaction (k_{en}) is 2 to 3 times faster than the corresponding process for the EDTA complex, although the latter involves more kinetically equivalent paths. It is concluded that the crowding associated with the peripheral methyl group stabilizes the five-coördinate intermediate.

Acknowledgment.—The financial support of the National Science Foundation is gratefully acknowledged.

(24) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.* **78**, 716 (1956).

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Infrared Investigation of Certain Imidazole Derivatives and their Metal Chelates[1]

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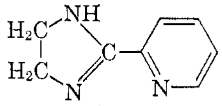
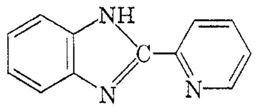
The infrared spectra of 2-(2-pyridyl)-imidazoline, 2-(2-pyridyl)-benzimidazole, 2-(*o*-hydroxyphenyl)-imidazoline, 2-(*o*-hydroxyphenyl)-benzimidazole, and their metal chelates have been measured in the region between 5000 and 300 cm.$^{-1}$. The observed bands are assigned by comparison with the frequencies of imidazole, of 1,2-dichloroethane, and of *ortho*-disubstituted benzene and pyridine for which normal coördinate analysis has been done. The spectra of metal chelates are interpreted by correlation with those of the ligands. The infrared spectra can be reasonably explained on the basis of the usually accepted structure in which chelation takes place through the unsaturated nitrogen atom and through the nitrogen atom of the pyridine ring or the phenolic oxygen atom. Assignments of metal–oxygen and metal–nitrogen stretching frequencies are made by comparing the spectra of the ligands with those of their metal chelates.

Introduction

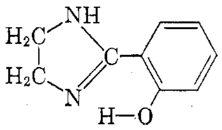
Previous work on the infrared spectra of imidazole derivatives and their metal chelates dealt primarily with assignments of the bands in the 3-μ region in order to observe the effect of coördination on the N–H stretching frequency.[3] A further study was desirable because these compounds are becoming increasingly more important as analytical, biochemical, and anticancer reagents. In the present investigation the infrared spectroscopic measurements of 2-(2-pyridyl)-imidazoline (I), 2-(2-pyridyl)-benzimidazole (II), 2-(*o*-hydroxyphenyl)-imidazoline (III), and 2-(*o*-hydroxyphenyl)-benzimidazole (IV) and their Cu(II), Ni(II), Co(II), and Zn(II) chelates was undertaken in the 2–35-μ region in order to make



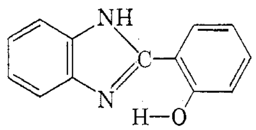
I



II



III



IV

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(1) Presented in part at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1961.

(2) Faculty of Science, University of Tokyo, Tokyo, Japan. Research Associate at the University of Notre Dame, summer of 1960.

(3) T. R. Harkins, J. L. Walter, O. E. Harris, and H. Freiser, *J. Am. Chem. Soc.*, **78**, 260 (1956).

a more complete assignment of the observed bands and to investigate the effect of metal binding on the characteristic frequencies of these compounds.

Experimental

Materials.—Imidazole was obtained from the Upjohn Company, Kalamazoo, Michigan, and was purified by recrystallization.

2-(2-Pyridyl)-imidazoline and 2-(2-pyridyl)-benzimidazole were prepared by condensing α-picolinic acid with ethylenediamine and *o*-phenylenediamine, respectively. 2-(*o*-Hydroxyphenyl)-imidazoline and 2-(*o*-hydroxyphenyl)-benzimidazole similarly were obtained by condensing salicylamide with ethylenediamine and *o*-phenylenediamine, respectively. The experimental details have been reported in the literature.[4-7]

Anal. 2-(2-Pyridyl)-imidazoline, calcd. for $C_8H_9N_3$: C, 65.31; H, 6.12; N, 28.57. Found: C, 64.82; H, 6.20; N, 28.32. 2-(2-Pyridyl)-benzimidazole, calcd. for $C_{12}H_9N_3$: C, 73.85; H, 4.62; N, 21.54. Found: C, 73.64; H, 4.68; N, 21.75. 2-(*o*-Hydroxyphenyl)-imidazoline, calcd. for $C_9H_{10}N_2O$: C, 66.67; H, 6.17; N, 17.28. Found: C, 66.44; H, 6.25; N, 17.20. 2-(*o*-Hydroxyphenyl)-benzimidazole, calcd. for $C_{13}H_{10}N_2O$: C, 74.30; H, 4.76; N, 13.33. Found: C, 74.42; H, 4.70; N, 13.60.

The metal chelates were prepared by the method described by Harkins, *et al.*[3]

Anal. 2-(2-Pyridyl)-imidazoline chelates, calcd. for $Ni(C_8H_9N_3)_3I_2$: C, 38.21; H, 3.58; N, 16.72. Found: C, 38.62; H, 3.69; N, 16.41. Calcd. for $Co(C_8H_9N_3)_3I_2$: C, 38.20; H, 3.58; N, 16.71. Found: C, 38.31; H, 3.60; N, 16.72. Calcd. for $Zn(C_8H_9N_3)_2Br_2$: C, 36.97; H, 3.47; N, 16.17. Found: C, 37.06; H, 3.46; N, 16.27. 2-(2-Pyridyl)-benzimidazole chelates, calcd. for $Cu(C_{12}H_9N_3)_2Br_2$: C, 46.94; H, 2.93; N, 13.69. Found: C, 46.75; H, 2.95; N, 13.80. Calcd. for $Ni(C_{12}H_9N_3)_3Br_2$: C, 53.75; H, 3.36; N, 15.68. Found: C, 53.86; H, 3.39; N, 15.50. Calcd. for $Co(C_{12}H_9N_3)_3Br_2$: C, 53.74; H, 3.36; N, 15.67. Found: C, 53.90; H, 3.40; N, 15.52. Calcd. for $Zn(C_{12}H_9N_3)_2I_2$: C, 40.60; H, 2.54; N, 11.84. Found: C, 40.89; H, 2.59; N, 12.06. 2-(*o*-Hydroxyphenyl)-imidazoline chelates, calcd. for $Cu(C_9H_9N_2O)_2$: C, 56.03; H, 4.67; N, 14.53. Found: C, 56.52; H, 4.74; N, 14.75. Calcd. for $Ni(C_9H_9N_2O)_2$: C, 56.74; H, 4.73; N, 14.71. Found: C, 57.21; H, 4.79; N, 14.96. Calcd. for $Zn(C_9H_9N_2O)_2$: C, 55.76; H, 4.65; N, 14.46. Found: C, 56.81; H, 4.71; N, 13.84. 2-(*o*-Hydroxyphenyl)-benzimidazole chelates, calcd. for $Cu(C_{13}H_9N_2O)_2$: C, 64.80; H, 3.74; N, 11.63. Found: C, 64.01; H, 3.68; N, 11.34. Calcd. for $Co(C_{13}H_9N_2O)_2$: C, 65.42; H, 3.77; N, 11.74. Found: C, 64.83; H, 3.73; N, 12.11. Calcd. for $Zn(C_{13}H_9N_2O)_2$: C, 64.54; H, 3.72; N, 11.58. Found: C, 64.01; H, 3.78; N, 11.96.

Measurements of Infrared Spectra.—The spectra were obtained by using a Perkin–Elmer Model 21 infrared spectrophotometer, using NaCl (3–15 μ), CaF_2 (2–5 μ), and CsBr (15–37 μ) prisms. Samples were prepared in KBr disks and their spectra checked by Nujol mulls and dilute chloroform solutions. Wave length calibration was made using polystyrene (in the NaCl region) and pure rotation spectral lines of water vapor (in the CsBr region).

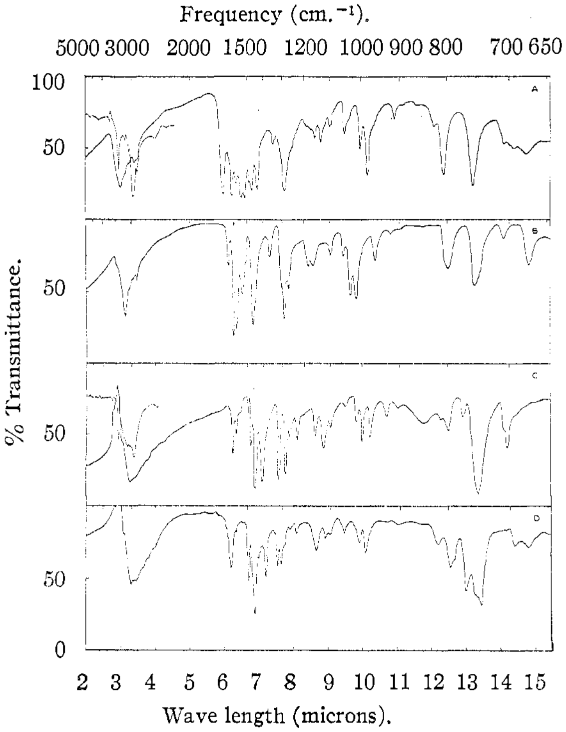

Fig. 1—Infrared absorption curves in the NaCl region of (A) 2-(2-pyridyl)-imidazoline, (B) 2-(2-pyridyl)-imidazolineCo(II)iodide, (C) 2-(2-pyridyl)-benzimidazole, (D) 2-(2-pyridyl)-benzimidazoleCu(II) bromide (—in KBr, ... dilute solution in chloroform).

The spectra of the ligands and of one typical metal chelate in the NaCl region appear in Fig. 1 and 2. In Fig. 3 and 4 are given the spectra of the 2-(*o*-hydroxyphenyl) derivatives and their metal chelates in the CsBr region.[8] The frequencies and the intensities of the observed bands and the assignments of these bands are listed in Tables I–IV.

Discussion

For the type of compounds under investigation there is sufficient experimental evidence to indicate that coördination takes place through the unsaturated nitrogen atom and not through the imino nitrogen.[9] Accordingly, the metal chelates have been assigned the structures V and VI. The infrared spectra obtained for these compounds can be reasonably discussed and explained on the basis of these structures.

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

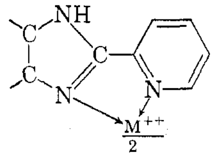
(5) A. Leko and G. Vlajinats, *Bull. soc. chim. roy. Yougoslav.*, **1**, 3 (1930).

(6) D. W. Hein, R. J. Alheim, and J. J. Leavitt, *J. Am. Chem. Soc.*, **79**, 427 (1957).

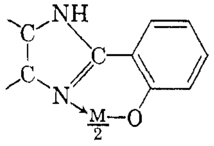
(7) J. L. Walter and H. Freiser, *Anal. Chem.*, **25**, 127 (1953).

(8) No definite information could be obtained from the spectra of the metal chelates of the 2-(2-pyridyl) derivatives in the CsBr region.

(9) (a) L. Hunter and J. A. Marriot, *J. Chem. Soc.*, 777 (1941); (b) T. J. Lane and K. P. Quinlan, *J. Am. Chem. Soc.*, **82**, 2994 (1960).



V



VI

(A) **5–7-μ Region.**—In this region, the C=N stretching, the N–H in-plane deformation, the CH_2 scissors, and some of the pyridine and benzene ring vibrations are expected as fundamentals.[10,11] In open chain compounds and in non-conjugated ring systems the C=N stretching frequency usually is observed at about 1650 cm.$^{-1}$. However, this band undergoes considerable change in intensity and in frequency depending upon the nature of the attached groups. In the type of molecules under study, the presence of the aromatic rings and of the N–H group which give absorptions in the same region also could affect the C=N stretching frequency due to coupling. Therefore, to facilitate an understanding of the frequencies in the spectra of these molecules the vibrational assignments in this region of a simpler molecule, imidazole, are discussed first.

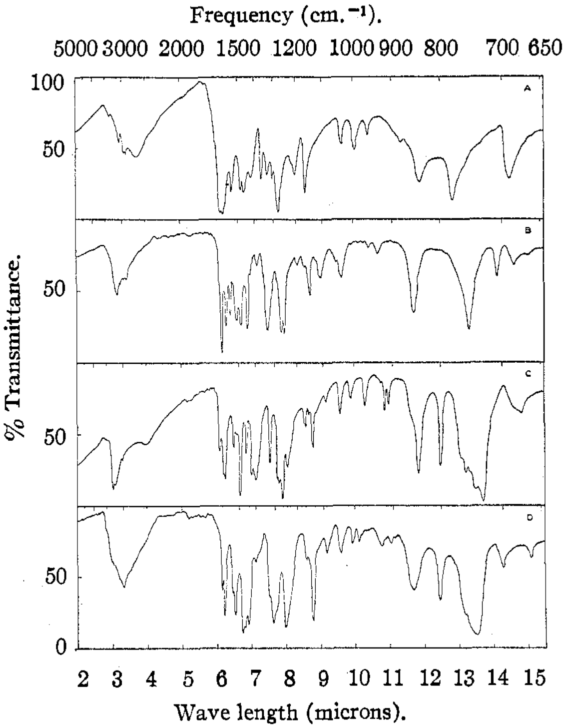


Fig. 2—Infrared absorption curves in KBr in the NaCl region of (A) 2-(*o*-hydroxyphenyl)-imidazoline, (B) 2-(*o*-hydroxyphenyl)-imidazolineCu(II) chelate, (C) 2-(*o*-hydroxyphenyl)-benzimidazole, (D) 2-(*o*-hydroxyphenyl)-benzimidazole Zn(II) chelate.

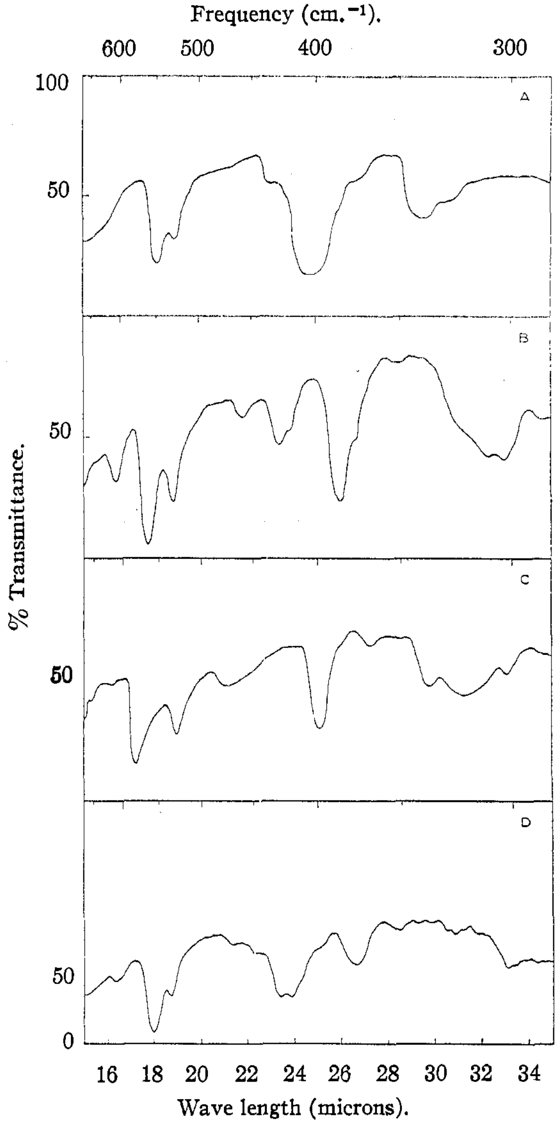


Fig. 3—Infrared absorption curves in KBr of 2-(*o*-hydroxyphenyl)-imidazoline and its chelates in the CsBr region: (A) ligand, (B) Cu(II) chelate, (C) Ni(II) chelate, (D) Zn(II) chelate.

In imidazole, absorption peaks are observed at 1828, 1675, 1582, 1548, 1499, 1488, and 1451 cm.$^{-1}$, in agreement with the values reported by Otting.[12] The weak band in the solid state at 1828 cm.$^{-1}$ almost disappears in dilute chloroform solution. The peak at 1675 cm.$^{-1}$ in the solid state shifts to 1647 cm.$^{-1}$ in chloroform solution and decreases in intensity on dilution. Both these peaks therefore probably are related to the associated molecule. The band at 1548 cm.$^{-1}$ which disappears on deuteration is assigned

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[10] W. West, "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956.

[11] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

[12] W. Otting, *Chem. Ber.*, **89**, 2887 (1956).

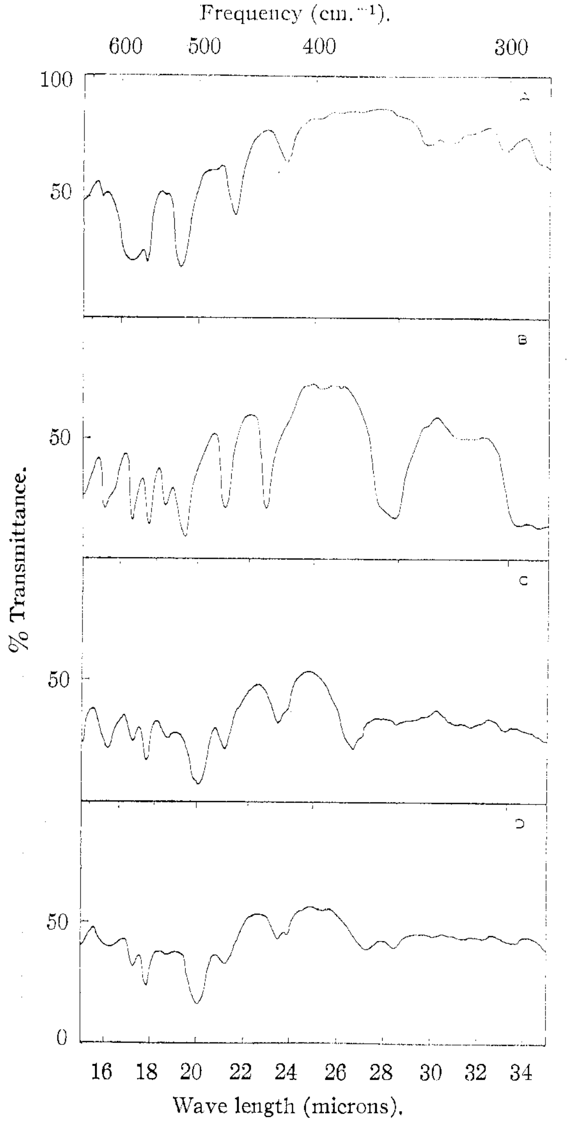

Fig. 4—Infrared absorption curves in KBr of 2-(*o*-hydroxyphenyl)-benzimidazole and its chelates in the CsBr region: (A) ligand, (B) Cu(II) chelate, (C) Co(II) chelate, (D) Zn(II) chelate.

to the N–H in-plane deformation vibration. The peak at 1582 cm.$^{-1}$ in the solid state is shifted to 1595 cm.$^{-1}$ in chloroform solution and can be assigned to the antisymmetric C═N—C═C stretching vibration. One of the three remaining peaks at 1499, 1484, and 1451 cm.$^{-1}$ can be assigned to the symmetric C═N—C═C stretching vibration. Most probably the strong peak at 1451 cm.$^{-1}$ arises from this mode and the other two can be explained as overtone or combination bands. In the spectrum of the coördination complex of imidazole with Cu(II) ion, the peaks at 1582 and 1451 cm.$^{-1}$ are shifted to 1605 and 1440 cm.$^{-1}$, respectively.

(a) **2-(2-Pyridyl)-imidazoline.**—The C═N stretching frequency, probably somewhat coupled with the pyridine ring vibration, shows up as a strong peak at 1664 cm.$^{-1}$. This frequency does not change appreciably on deuteration and hence may not be coupled with the N–H in-plane deformation mode. On chelation, this frequency is lowered to 1634, 1631, and 1631 cm.$^{-1}$ in Ni(II), Co(II), and Zn(II), respectively. This shift can be explained on the basis of structure V.

The band at 1506 cm.$^{-1}$ is assigned to the N–H in-plane deformation vibration since no corresponding peak is observed in the spectrum of the deuterated species.

The other peaks in the region between 1450 and 1600 cm.$^{-1}$ arise mainly from pyridine ring vibrations. Possibly some of these of weak intensities are due to combination bands or overtones. These peaks do not undergo any appreciable change on chelation of the ligand with metal ions.

The peak at 1429 cm.$^{-1}$ is assigned to the CH_2 scissors motion[13] while that at 1460 cm.$^{-1}$ probably also can be assigned to the same vibration.

(b) **2-(2-Pyridyl)-benzimidazole.**—A comparison of the spectrum of the ligand with those of its metal chelates shows that very little change in the frequencies is brought about in this region by chelation. This may be due to the presence of additional aromatic rings in these compounds, which results in greater coupling and conjugation.

(c) **2-(*o*-Hydroxyphenyl)-imidazoline.**—In the spectrum of this compound the peaks at 1477 and 1456 cm.$^{-1}$ can be definitely assigned to the vibrations of the *ortho*-disubstituted benzene ring.[14] On chelation these frequencies are shifted to higher values. The peak at 1477 cm.$^{-1}$ is shifted to 1513, 1511, and 1508 cm.$^{-1}$ and the one at 1456 cm.$^{-1}$ to 1481, 1484, and 1484 cm.$^{-1}$ in the Cu(II), Ni(II), and Zn(II) chelates, respectively.

Two very strong peaks are observed at 1621 and 1600 cm.$^{-1}$ in the spectrum of 2-(*o*-hydroxyphenyl)-imidazoline, one of which is due to the C═N stretching vibration and the other to the *ortho*-disubstituted benzene ring vibration.[10,11,14] Although these two vibrations are coupled with each other, it is reasonable to assign the peak at 1621 cm.$^{-1}$ primarily to the C═N stretching vibration since in the metal chelates this frequency is lowered to 1582 [Cu(II)], 1590 [Ni(II)], and 1577

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[13] I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 589 (1955).

[14] Y. Kakiuti, *Kagaku no Ryôiki*, **No. 8**, 1 (1959).

TABLE I

ABSORPTION FREQUENCIES IN 2-(2-PYRIDYL)-IMIDAZOLINE (P) AND METAL CHELATES[a]

P in KBr	P in $CHCl_3$	P_3NiI_2	P_3CoI_2	P_2ZnBr_2	Assignment
3328 (s)	3425 (s)				N–H str.
		3185 (s)	3190 (s)	3186 (s)	N–H str. in chelate
3051 (w)	3067 (w)	3049 (w)	3049 (w)	3049 (w)	C–H str.
2928 (w)	2959 (s)	2924 (w)	2976 (w)	2933 (w)	C–H str.
2841 (w)	2882 (m)	2857 (w)	2865 (w)	2882 (w)	C–H str.
1664 (s)	1672 (v.s)	1634 (m)	1631 (m)	1631 (m)	C=N str.
	1621 (s)				
1595 (s)	1603 (m)	1590 (s)	1585 (s)	1587 (s)	Pyr. ring vib.
1567 (m)	1577 (m)	1567 (s)	1567 (s)	1567 (s)	Pyr. ring vib.
1546 (sh)	1548 (sh)				
1531 (s)	1531 (s)	1531 (m)	1533 (m)	1538 (m)	
1506 (s)	1499 (s)	1520 (sh)	1522 (sh)	1527 (sh)	N–H in plane def.
1477 (sh)	1479 (sh)				
1460 (s)	1460 (s)	1453 (s)	1453 (s)	1460 (s)	CH_2 scissors
1429 (s)	1425 (s)	1439 (sh)	1439 (sh)	1439 (m)	CH_2 scissors
1340 (w)	1340 (w)	1359 (w)	1357 (w)	1361 (w)	CH_2 wagging
		1299 (sh)	1299 (sh)	1300 (w)	
1280 (s)	1287 (s)	1289 (s)	1282 (s)	1285 (m)	*o*-Subst. pyr.
1247 (sh)	1241 (m)	1266 (m)	1264 (m)	1269 (sh)	
1178 (sh)	1181 (w)	1181 (w)	1179 (m)	1183 (w)	
1167 (v.w)					
1151 (w)	1149 (w)	1160 (m)	1157 (m)	1163 (w)	*o*-Subst. pyr.
1127 (m)	1127 (m)				
1094 (w)	1094 (m)	1096 (w)	1095 (m)	1093 (w)	
1046 (m)	1045 (m)	1054 (w)	1053 (m)	1055 (w)	*o*-Subst. pyr.
		1032 (m)	1029 (s)	1031 (m)	
996 (m)	999 (s)	1012 (m)	1010 (s)	1010 (m)	Pyr. ring breathing
978 (s)	981 (s)	959 (m)	957 (m)	967 (m)	
907 (m)	905 (w)				CH_2 rocking (2 peaks)
822 (m)	820 (m)				
804 (s)	798 (m)	797 (m.b)	796 (m.b)	802 (s)	N–H out-of-plane def.
752 (s)		752 (s)	750 (s)	752 (sh)	C–H out-of-plane def.
		745 (s)	743 (sh)	749 (s)	C–H out-of-plane def.
706 (m)	701 (m)	705 (w)	705 (w)	704 (w)	
674 (m.b)	676 (m.b)	669 (m)	671 (m)	675 (m)	

[a] Abbreviations: P = 2-(2-pyridyl)-imidazoline; s = strong; m = medium; w = weak; sh = shoulder; b = broad; v = very.

cm.$^{-1}$ [Zn(II)]. The value of 1621 cm.$^{-1}$ is lower than that of the C=N stretching frequency in 2-(2-pyridyl)-imidazoline (1664 cm.$^{-1}$), but this lowering can be attributed to strong intramolecular hydrogen bonding between the unsaturated nitrogen atom and the hydrogen of the hydroxyl group.

The peak at 1600 cm.$^{-1}$ now can be assigned primarily to the benzene ring vibration. As in the case of the benzene ring vibrations at 1477 and at 1456 cm.$^{-1}$, the frequency of the vibration at 1600 cm.$^{-1}$ is increased upon chelation and the peak is observed at 1618, 1621, and 1610 cm.$^{-1}$ in the Cu(II), Ni(II), and Zn(II) chelates, respectively.

The peak at 1412 cm.$^{-1}$ can be assigned definitely to the CH_2 scissors vibration.[13] Another CH_2 scissors mode may be considered superimposed on the peak at 1456 cm.$^{-1}$ in the ligand (Table III).

The only remaining peak in this region, the one at 1537 cm.$^{-1}$, is assigned to the N–H in-plane deformation vibration. In the spectra of the chelates there is a slight shift in the frequency of this peak but this is not attributed to chelation effects since coördination does not take place through the imino nitrogen.

(d) **2-(*o*-Hydroxyphenyl)-benzimidazole.**—The peak observed at 1634 cm.$^{-1}$ is lowered on chelation to 1626 [Cu(II)], 1628 [Co(II)], and 1631 cm.$^{-1}$ [Zn(II)] and is assigned to the C=N stretching vibration primarily. The shift is much less significant than in the case of 2-(*o*-hydroxyphenyl)-imidazoline.

The peaks observed at 1595, 1499, 1456, and 1425 cm.$^{-1}$ are due to the vibrations of the *ortho*-

Table II

Absorption Frequencies in 2-(2-Pyridyl)-benzimidazole (PB) and Metal Chelates[a]

PB in KBr	(PB)$_2$CuBr$_2$	(PB)$_3$NiBr$_2$	(PB)$_3$CoBr$_2$	(PB)$_2$ZnI$_2$	Assignment
3430^c					N–H str.
3247 (sh)	3275(w)	3284 (w)	3265 (w)	3263 (w)	N–H str.
3049 (s.b)	3055 (s)	3044 (s)	3046 (s)	3024 (s)	C–H str.
1629 (sh)					
1603 (m)	1613 (m)	1610 (m)	1609 (m)	1605 (m)	
1575 (m)	1575 (w)	1576 (w)	1573 (w)	1575 (w)	C=N str.,
1546 (v.w)					Pyr. ring vib.,
1493 (m)					Benz. ring vib.,
1475 (m)	1488 (m)	1488 (m)	1482 (m)	1488 (m)	N–H in-plane def.
	1453 (sh)	1458 (m)	1454 (sh)	1458 (sh)	
1449 (v.s)	1449 (s)	1446 (s)	1444 (s)	1445 (s)	
1406 (s)	1389 (m)	1388 (m)	1386 (m)	1387 (m)	
1319 (s)	1325 (m)	1324 (m)	1321 (m)	1321 (m)	
1283 (s)	1307 (m)	1305 (m)	1300 (m)	1302 (m)	*o*-Subst. pyr. vib.
	1292 (sh)	1286 (v.w)	1282 (w)	1287 (sh)	
1263 (m)	1264 (w)	1263 (v.w)	1261 (w)	1263 (w)	
1230 (m)	1233 (w)	1230 (w)	1230 (w)	1232 (w)	
1153 (m)	1152 (m)	1151 (m)	1149 (m)	1151 (m)	*o*-Subst. pyr. vib.
1121 (m)	1120 (w)	1117 (w)	1117 (w)	1121 (m)	
1096 (m)	1103 (w)	1099 (w)	1096 (w)	1095 (w)	
1046 (w)	1054 (w)	1053 (w)	1053 (w)	1053 (w)	*o*-Subst. pyr. vib.
1013 (m)	1016 (sh)	1019 (w)	1015 (sh)	1019 (w)	
996 (m)	1007 (m)	1010 (m)	1006 (m)	1005 (m)	Pyr. ring breathing
973 (m)	988 (m)	980 (m)	978 (m)	980 (m)	
929 (w)	933 (v.w)	930 (v.w)	930 (v.w)	930 (v.w)	C–H out-of-plane def. of benz. ring
846 (m.b)	818 (m)	816 (m)	815 (m)	815 (m)	
797 (m)	796 (m)	794 (m)	792 (m)	794 (m)	N–H out-of-plane def.
770 (m)	766 (m)	764 (m)	763 (m)	762 (m)	C–H out-of-plane def. of benz. ring
744 (v.w)	741 (s)	744 (s.b)	745 (s.b)	745 (s.b)	C–H out-of-plane def. of pyr. ring
701 (m)	693 (m) 673 (m)	692 (m)	691 (m)	692 (m)	

[a] Abbreviations: PB = 2-(2-pyridyl)-benzimidazole; c = dilute solution in CHCl$_3$; s = strong; m = medium; w = weak; sh = shoulder; b = broad; v = very.

disubstituted benzene rings.[14] These frequencies do not change appreciably in the spectra of the chelates.

(B) 7–15-μ Region.—In this region, a study of the N–H out-of-plane deformation vibration and the O–H in-plane deformation vibration of the ligands and the M–O stretching vibration of the chelates is helpful in understanding the effects of chelation.

(a) 2-(2-Pyridyl)-imidazoline.—The peaks at 1280, 1151, 1046, and 996 cm.$^{-1}$ are characteristic vibrations of the *ortho*-substituted pyridine component and correspond to similar vibrations observed for α-picoline at 1290, 1147, 1049, and 998 cm.$^{-1}$.[15] The peak at 996 cm.$^{-1}$ is assigned to the pyridine breathing mode. On chelation it shifts to 1012 [Ni(II)], 1010 [Co(II)], and 1010 cm.$^{-1}$ [Zn(II)]. Such a shift is explained by the fact that the nitrogen atom of the pyridine ring donates a pair of electrons to the metal ion forming a coördinate covalent bond.

Another characteristic vibration of the *ortho*-substituted pyridine rings is the C–H out-of-plane motion. The peak at 752 cm.$^{-1}$ is assigned to this mode. (In α-picoline, the corresponding band is at 749 cm.$^{-1}$.[14,15a]) On chelation with metal ions these hydrogen vibrations will not be considerably affected and hence this frequency is not altered in the spectra of the chelates.

The peak at 804 cm.$^{-1}$ is shifted on deuteration and therefore is assigned to the N–H out-of-plane deformation vibration. On chelation this frequency does not undergo any appreciable change. This observation may be considered as constituting spectroscopic evidence that chelation does

(15) (a) H. Shindo, *Pharm. Bull.*, **5**, 472 (1957); (b) R. R. Randle and D. M. Whiffen, *Trans. Faraday Soc.*, **52**, 9 (1936).

TABLE III

ABSORPTION FREQUENCIES IN 2-(*o*-HYDROXYPHENYL)-IMIDAZOLINE (RH) AND METAL CHELATES[a]

RH in KBr	R_2Cu	R_2Ni	R_2Zn	Assignment
3375 (m)				N–H str.
	3160 (s)	3178 (s)	3172 (s)	N–H str. in chelates
3044 (m)	3049 (w)	3044 (w)	3049 (sh)	C–H str.
2922 (m)	2924 (m)	2930 (w)	2933 (sh)	
2874 (m)	2882 (m)	2882 (w)	2890 (m)	
2784 (sh)				
2690 (m.b)				Bonded O–H str.
1621 (v.s)	1582 (m)	1590 (s)	1577 (v.s)	C=N str.
1600 (v.s)	1618 (v.s)	1621 (v.s)	1610 (v.s)	Benzene ring vib.
1537 (m)	1552 (m)	1555 (m)	1541 (s)	N–H in-plane def.
1513 (sh)				
1477 (m)	1513 (m)	1511 (s)	1508 (s)	*o*-Disubst. benz. ring vib.
1456 (m)	1481 (m)	1484 (m)	1484 (s)	
[1456 (m)]	1443 (m)	1445 (s)	1439 (s)	CH_2 scissors
1412 (m)	1418 (w)	1425 (sh)	1420 (sh)	
	1381 (w)	1377 (w)	1370 (m)	
1355 (m)				O–H in-plane def.
1321 (m)	1333 (s)	1328 (s)	1333 (s)	C–H in-plane def. of benzene ring, vibrations of imidazoline ring including CH_2 wagging and twisting vibrations, C–O str.
1299 (m)	1311 (sh)	1312 (sh)	1309 (sh)	
1272 (s)	1266 (s)	1266 (s)	1261 (s)	
	1252 (s)	1258 (s)	1241 (s)	
1198 (m)	1190 (w)	1193 (w)	1195 (w)	
	1166 (sh)	1164 (w)	1167 (m)	
1156 (s)	1144 (m)	1145 (m)	1147 (m)	
	1105 (m)	1101 (m)	1117 (w)	
	1052 (sh)	1054 (w)	1054 (sh)	
1031 (m)				
993 (m)	1034 (m)	1036 (m)	1042 (m)	Benz. ring breathing
956 (m)	956 (w)	960 (v.w)	956 (w)	C–H out-of-plane def. in *o*-disubst. benz.
	933 (w)	933 (w)	932 (v.w)	
877 (m)				CH_2 rocking
836 (m)	851 (m)	858 (m)	846 (s)	C–H out-of-plane def. in *o*-disubst. benz., N–H out-of-plane def.
744 (s)	749 (s)	746 (s)	749 (s)	
	706 (m)	704 (m)	708 (m)	M–O str.
686 (m)	681 (w)	678 (m)	686 (m)	C–H out-of-plane def. in *o*-disubst. benz.
	610 (m)		608 (w)	
551 (s)	569 (s)	580 (s)	555 (s)	
527 (m)	531 (m)	527 (m)	535 (m)	
434 (w)	459 (w)	472 (w)	469 (v.w)	
			448 (v.w)	
419 (s)	428 (m)	398 (s)	427 (s)	
	422 (sh)		418 (s)	
	384 (s)	367 (w) or 336 (m)	374 (s)	M–N str.
340 (m)	309 (s)		351 (v.w)	
336 (m)	302 (s)	320 (m)	302 (m)	

[a] Abbreviations: RH = 2-(*o*-hydroxyphenyl)-imidazoline; s = strong; m = medium; w = weak; sh = shoulder; v = very; b = broad.

not take place through the imino nitrogen.[16]

The remaining peaks observed in this region arise from the vibrations of the imidazoline ring. Of these, the band at 1340 cm.$^{-1}$ is assigned to the CH_2 wagging vibration and two of the three peaks at 978, 907, and 822 cm.$^{-1}$ are assigned to the CH_2 rocking vibration.[13, 17]

(b) 2-(2-Pyridyl)-benzimidazole.—The peaks at 1283, 1153, 1046, and 996 cm.$^{-1}$ are character-

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[16] If chelation took place through the imino nitrogen, the electron density of this nitrogen atom would change and the N–H deformation frequency would be remarkably affected.

[17] I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953).

TABLE IV

ABSORPTION FREQUENCIES IN 2-(*o*-HYDROXYPHENYL)-BENZIMIDAZOLE (R^1H) AND METAL CHELATES[a]

R^1H in KBr	$(R^1)_2Cu$	$(R^1)_2Co$	$(R^1)_2Zn$	Assignment
	3390 (sh)	3393 (sh)	3394 (w)	
3333 (s)				N–H stretching
3247 (s)				
3050 (m)	3086 (s)	3053 (s)	3055 (s)	N–H str. in chelates, C–H stretching
	2907 (m)	2906 (w)	2890 (m)	
2540				Bonded O–H str.
1634 (m)	1626 (m)	1628 (m)	1631 (m)	C=N str.
1605 (sh)				
1595 (s)	1608 (s)	1610 (s)	1608 (s)	*o*-Disubst. benzene ring vib.
	1555 (m)	1557 (m)	1555 (sh)	
1538 (m)	1536 (m)	1530 (s)	1531 (s)	N–H in-plane def.
1516 (sh)				
1499 (v.s)	1481 (v.s)	1480 (v.s)	1481 (v.s)	*o*-Disubst. benzene ring vib.
	1464 (s)	1463 (s)	1463 (sh)	
1456 (m)	1447 (s)	1446 (s)	1446 (s)	
1425 (m)	1409 (v.w)	1405 (w)	1404 (w)	
1397 (s)				O–H in-plane def.
	1388 (w)	1388 (sh)	1388 (sh)	Benzene ring breathing vib., C–H in-plane def. of benzene ring, vibrations of imidazole ring, C–O str., N–H out-of-plane def., C–H out-of-plane def. in *o*-disubst. benzene
	1332 (sh)	1328 (sh)	1330 (sh)	
1321 (m)	1317 (s)	1312 (s)	1311 (s)	
1277 (s)	1280 (sh)	1290 (sh)	1291 (sh)	
1262 (s)	1261 (v.s)	1253 (s)	1250 (v.s)	
1239 (m)	1226 (sh)			
1163 (m)	1166 (w)	1163 (w)	1164(w)	
1167 (w)				
1134 (m)	1143 (s)	1139 (s)	1140 (s)	
1120 (sh)	1117 (sh)	1117 (sh)	1117 (sh)	
1086 (w)	1096 (w)	1089 (w)	1091 (w)	
1038 (m)	1041 (m)	1042 (m)	1045 (m)	
1007 (w)	1011 (w)	1007 (w)	1009 (w)	
	984 (w)	987 (v.w)	990 (w)	
966 (m)	965 (v.w)	962 (v.w)	964 (v.w)	
916 (m)	928 (w)	929 (v.w)	930 (w)	
907 (m)	907 (w)	906 (w)	907 (w)	
841 (s)	860 (s)	858 (m)	858 (m)	
799 (s)	807 (m)	805 (m)	805 (m)	
761 (sh)	762 (sh)	759 (sh)	758 (sh)	
754 (s)				
738 (sh)	734 (s)	738 (s)	738 (s)	
726 (v.s)				
	704 (w)	699 (w)	701 (m)	M–O str.
671 (m)	665 (w)	664 (w)	664 (m)	
630 (w)	627 (m)	620 (m)	620 (w.b)	
584 (s)	583 (m)	580 (m)	579 (m)	
562 (s)	560 (m)	560 (m)	560 (m)	
539 (v.w)	539 (w)	535 (w)	535 (v.w)	
520 (s)	516 (s)	499 (s)	499 (s)	
464 (m)	472 (s)	472 (m)	470 (m)	
420 (m)	437 (s)	425 (m)	425 (m)	
	355 (v.s)	378 (s)	367 (m)	M–N str.
336 (w)		370 (sh)		

[a] Abbreviations: R^1H = 2-(*o*-hydroxyphenyl)-benzimidazole; s = strong; m = medium; w = weak; sh = shoulder; v = very; b = broad.

istic vibrations of the *ortho*-substituted pyridine ring,[15] as has been discussed for 2-(2-pyridyl)-imidazoline. The slight increase on chelation in the frequency of the pyridine breathing vibration (996 cm.$^{-1}$) can be attributed to coördination from the pyridine nitrogen to the metal ion. The peak at 744 cm.$^{-1}$ is assigned to the C–H out-of-plane deformation vibration of the pyridine ring.[15] The peaks at 929 and 770 cm.$^{-1}$ are assigned to the C–H out-of-plane deformation vibration of the *ortho*-disubstituted benzene ring.[14] The peak at 797 cm.$^{-1}$, as in the case of 2-(2-pyridyl)-imidazoline, is assigned to the N–H out-of-plane deformation vibration and is not altered on chelation since coördination does not take place through the imino nitrogen atom.

(c) **2-(*o*-Hydroxyphenyl)-imidazoline.**—The peak at 1355 cm.$^{-1}$ which disappears in the metal chelates is assigned to the O–H in-plane deformation vibration.[18] The peak at about 1380 cm.$^{-1}$ in the spectra of the chelates is too weak to correspond to the strong peak at 1355 cm.$^{-1}$ in the ligand and may be explained as a combination band or as an overtone.

In each of the spectra of the metal chelates a band of medium intensity is observed at 706, 704, and 708 cm.$^{-1}$ for Cu(II), Ni(II), and Zn(II), respectively. This does not correspond to any peak in the ligand in this region and hence is assigned to the metal–oxygen stretching vibration.

The peak at 993 cm.$^{-1}$ is assigned to the benzene ring breathing vibration.[11,19] In the chelates this shifts to higher frequencies.

The peaks at 956, 836, 744, and 686 cm.$^{-1}$ correspond to the four characteristic peaks of *o*-cresol and are assigned to the C–H out-of-plane deformation vibration of the *ortho*-disubstituted benzene ring.

The N–H out-of-plane deformation vibration of the imidazoline ring probably is overlapped by the strong peak at 744 or 836 cm.$^{-1}$. The peak at 877 cm.$^{-1}$ is assigned to the CH_2 rocking vibration.[17] The remaining peaks which are observed in the region between 1350 and 1000 cm.$^{-1}$ arise from the C–H in-plane deformation vibrations of the benzene ring, the vibrations of the imidazoline ring (including the CH_2 wagging and the CH_2 twisting), and the C–O stretching vibration.

(d) **2-*o*-Hydroxyphenylbenzimidazole.**—The strong peak at 1397 cm.$^{-1}$ which disappears in the metal chelates is assigned to the O–H in-plane deformation vibration.

A new peak is observed at 704, 699, and 701 cm.$^{-1}$ in the spectra of Cu(II), Co(II), and Zn(II) chelates, respectively. This is assigned to the metal–oxygen stretching vibration in each of these chelates. The frequency values are practically the same as those for the metal chelates of 2-(*o*-hydroxyphenyl)-imidazoline, indicating that the metal–oxygen bond is of almost the same strength in both ligands.

The other frequencies to be expected in this region are those due to the benzene ring vibrations (the benzene ring breathing vibration and the C–H in-plane and out-of-plane deformation vibrations), the imidazole ring vibrations, the C–O stretching vibration, and the N–H out-of-plane deformation vibration. The presence of three rings in the molecule leads to stronger coupling among these vibrational modes. These frequencies do not shift considerably on chelation.

(C) 15–35-μ Region. (a) **2-(*o*-Hydroxyphenyl)-imidazoline.**—The peaks observed in the ligand in this region arise from skeletal deformation vibrations. In the spectra of Cu(II) and Zn(II) chelates, strong peaks are observed at 384 and 374 cm.$^{-1}$, respectively. These are definitely new bands not observed in the ligand and are assigned to the metal–nitrogen stretching vibration. In the Ni(II) chelate this band is less definite, but the peak at 336 cm.$^{-1}$ or the weaker band at 367 cm.$^{-1}$ most probably can be assigned to the metal–nitrogen stretching vibration.

(b) **2-(*o*-Hydroxyphenyl)-benzimidazole.**—In the metal chelates new peaks are observed at 355 cm.$^{-1}$ [Cu(II)], 378 cm.$^{-1}$ [Co(II)], and 367 cm.$^{-1}$ [Zn(II)]. These do not correspond to any other peak in the ligand and are assigned to the metal–nitrogen stretching vibration. The frequencies are slightly lower than the corresponding metal–nitrogen stretching frequencies in 2-(*o*-hydroxyphenyl)-imidazoline indicating weaker metal–nitrogen bonds. This is consistent with the lower basicity of the donor nitrogen atom in 2-(*o*-hydroxyphenyl)-benzimidazole.[20]

(D) 3-μ Region. (a) **2-(2-Pyridyl)-imidazoline.**—The sharp peak at 3425 cm.$^{-1}$ in dilute chloroform solution and the peak at 3328 cm.$^{-1}$ in the solid state are assigned to the N–H stretching frequency. Free N–H stretching frequency usually is observed at about 3400 cm.$^{-1}$. The lowering of the frequency in the solid state can be attributed to intermolecular hydrogen bonding. In the metal chelates the N–H stretching frequency shifts to 3185, 3190, and 3186 cm.$^{-1}$ in Ni(II), Co(II), and Zn(II), respectively. Since coördination does not take place through the

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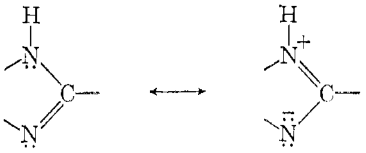
(18) Although it has been considered that the O–H in-plane deformation mode includes some component of the C–O stretching vibration, the detailed normal coördinate treatment of methanol [C. Tanaka, K. Kuratani, and S. Mizushima, *Spectrochim. Acta*, **9**, 265 (1957)] shows that the O–H in-plane deformation mode is almost pure. This essentially should be true also of phenols, although the benzene ring may cause a slight increase in the coupling of the C–O stretching mode.

(19) R. R. Randle and D. H. Whiffen, "Molecular Spectroscopy," The Institute of Petroleum, 1954, p. 111.

(20) W. D. Johnson and H. Freiser, *Anal. Chim. Acta*, **11**, 301 (1954).

imino nitrogen, the lowering of the N–H stretching frequency in the chelates can be explained by the resonance structures (VII, VIII) as has been discussed by Harkins, *et al.*[3] Donation of the pair of electrons from the unsaturated nitrogen to a metal ion would increase the contribution of structure VIII resulting in a lowering of the N–H stretching frequency. This is consistent with the results obtained by Quagliano[21] and Curran[22] for complexes containing NH_3 and $-NH_2$ groups.


VII VIII

(b) **2-(2-Pyridyl)-benzimidazole.**—The sharp peak at 3430 cm.$^{-1}$ in dilute chloroform solution is assigned to the free N–H stretching vibration. In the solid state spectrum of this compound the N–H stretching vibration is overlapped by the aromatic C–H stretching vibration and a broad peak is observed at 3049 cm.$^{-1}$. In the metal chelates this band is observed at 3055, 3044, 3046, and 3024 cm.$^{-1}$ in Cu(II), Ni(II), Co(II), and Zn(II), respectively.

(c) **2-(*o*-Hydroxyphenyl)-imidazoline.**—The peak at 3373 cm.$^{-1}$ is assigned to the N–H stretching vibration. This is higher than the value for 2-(2-pyridyl)-imidazoline, in which compound the N–H would be intermolecularly hydrogen bonded with the unsaturated nitrogen atom. The lowering of the frequency to 3160 cm.$^{-1}$ [Cu(II)], 3178 cm.$^{-1}$ [Ni(II)], and 3172 cm.$^{-1}$ [Zn(II)] in the metal chelates confirms the possibility of resonance contribution, as has been discussed.[3]

The broad peak at 2690 cm.$^{-1}$ is assigned to the O–H stretching vibration. No definite conclusions have been reached by spectroscopists as to the extent to which the O–H stretching frequency is lowered by hydrogen bonding. However, the broad nature of the peak and its absence in the chelates are indications that this peak may be due to the O–H stretching vibration. The low frequency is reasonable because in this compound strong intramolecular hydrogen bonding is expected between the pyridine-type nitrogen and the hydrogen atom of the O–H group.

(d) **2-(*o*-Hydroxyphenyl)-benzimidazole.**—The N–H stretching frequency appears as a doublet at 3333 and 3247 cm.$^{-1}$. In the chelates no definite peak at frequency values higher than 3100 cm.$^{-1}$ is observed. The broad peaks at 3086, 3053, and 3055 cm.$^{-1}$ in the Cu(II), Co(II), and Zn(II) chelates, respectively, probably are due to the N–H stretching frequency overlapped by the aromatic C–H stretching frequency.

The broad peak at 2540 cm.$^{-1}$, which does not appear in the chelates, is assigned, as above, to the bonded O–H stretching frequency.

The results of this infrared investigation are consistent with the other available data which show that in the type of ligands under study chelation takes place through the unsaturated nitrogen atom of the imidazole ring and through the pyridine nitrogen or the phenolic oxygen. The frequency shifts on chelation are larger in 2-(2-pyridyl)-imidazoline and in 2-(*o*-hydroxyphenyl)-imidazoline than in 2-(2-pyridylbenzimidazole) and in 2-(*o*-hydroxyphenol)-benzimidazole, indicating that the metal to ligand bonds are stronger in the derivatives of imidazoline than in those of benzimidazole. This is in agreement with the greater basicity of the unsaturated nitrogen atom in imidazoline than in benzimidazole.[20,23]

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(21) J. V. Quagliano, G. V. Svatos, and Br. C. Curran, *Anal. Chem.*, **26**, 429 (1959).

(22) Br. C. Curran, D. N. Sen, S. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **76**, 429 (1956).

(23) T. R. Harkins, Ph.D. Thesis, University of Pittsburgh, Pittsburgh, Pennsylvania, 1956.