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Pyrazolato and Related Anions.
Part III. Vibrational Assignments of Salts and Neutral Ligands

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Infrared and Raman spectra of salts of pyrazole (HPz), 4-chloropyrazole (HClPz), 4-bromopyrazole (HBrPz) and 4-iodopyrazole (HIPz) with transition metals are reported. Vibrational assignments of these salts are given and used for the interpretation of the infrared and Raman spectra of the neutral ligands.

Introduction

Previous papers [1, 2] in the present series dealt with the preparation and characterization of salts of pyrazole (HPz), 4-chloropyrazole (HClPz), 4-bromopyrazole (HBrPz) and 4-iodopyrazole (HIPz), with Cd(II), Zn(II), Co(II), Ni(II), Cu(II) and Co(III). Basically the formula of the salts is $M^{n+}(Pz)_n^-$, although in the case of Ni and Cu ammonia or water are also present. In this paper the results of a vibrational study are presented.

Infrared and Raman spectra of HPz have been tentatively assigned [3, 4]. A normal coordinate analysis of HPz has been published by Troitskaya [5]. Tentative assignments of HClPz and HBrPz only based on infrared spectra have been reported by Reedijk [6]. An assignment for HIPz was not available. Assignments of such neutral ligands are often uncertain, as a consequence of the low symmetry of the molecules in the solid state and of extensive coupling of N–H vibrations with other vibrations. For the pyrazolato ion the problem is less complex. The N–H vibrations are absent and the symmetry of the molecules will be higher, most probably C_{2v}. We therefore elaborated a vibrational assignment for the various pyrazolato ions, based on the infrared and Raman spectra of the zinc compounds. These results have been used subsequently to work out a vibrational assignment for the neutral molecules.

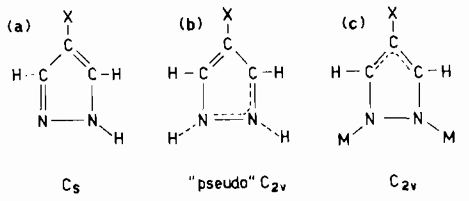
Experimental

The preparation of the neutral ligands and the salts has been described elsewhere [1, 2].

Infrared spectra were recorded on a Perkin Elmer 580 infrared spectrophotometer (4000–180 cm^{-1}), as nujol mulls and CsI pellets (wavenumber accuracy better than 2 cm^{-1}). Laser-Raman spectra were recorded on a JEOL JRS-4000 laser-Raman spectrophotometer equipped with a Coherent Radiation CR-2 Argon gas ion laser. No apparatus for depolarization measurements was available. Spectra of the solid compounds in capillaries were measured at both the 514.5 and 488.0 nm lines; CCl_4 served as a calibrant. Wavenumbers are believed to be accurate to 3 cm^{-1} in all regions. Raman spectra were recorded at the Vrije Universiteit in Amsterdam by Dr. M. W. G. de Bolster. $Zn(IPz)_2$ decomposed in the laser beam, therefore no Raman spectrum of this compound is available.

Empirical Assignment of the Observed Vibrations

The free neutral ligands belong to the C_s symmetry point group. As a consequence of hydrogen bonding in the solid state, the neutral molecules can be considered to possess C_{2v} symmetry, although not exactly as the N–H bonds are of different length (see formula *b*). As stated in Part I of this series the ligand ions are assumed to possess C_{2v} symmetry, in agreement with infrared and ligand field data. Assuming C_{2v} symmetry for the anion, a ten-atom system is sufficient to obtain the normal modes of vibration (see formula *c*). In this case 24 normal modes are expected.



Taking the Y-axis perpendicular to the plane, 9 A_1, 8 B_1, 3 A_2 and 4 B_2 modes are obtained in the case of C_{2v} symmetry. For C_s symmetry 17 A′ and 7 A″ modes are expected. All fundamentals are active in the Raman spectrum. Only the A_2 modes are infrared inactive.

TABLE I. Observed Infrared and Raman Bands in $Zn[Pz]_2$ and HPz.

$Zn[Pz]_2$				HPz	
IR	Raman	Assignment $Zn[Pz]_2$	IR range in other salts	IR	Raman [5]
178 m	180 s	A_1-fund			
270 s	260 s	A_1-fund	200–463		
300 s	290 sh	B_1-fund	495–240		
628 s		B_2-fund	625–636	618 s	627
670 vw	672 m	A_2-fund	670–682	655 m	
760 778 } s	780 w	B_2-fund	745–790	765 vs	782
843 vw	850 vw	A_2-fund	820–850	841 s	840
886 s	880 w	B_2-fund	880–892	894/882 s	880
922 m	920 m	A_1-fund	920–940	926/918 s	917
972 m	970 w	B_1-fund	960–980	938 s	944
1064 s	1060 w	B_1-fund	1055–1080	1035 s	1037
1075 sh		B_1-fund		1060 s	1050/1059
1167 s	1168 s	A_1-fund	1150–1180	1137 vs	
1182 sh		B_1-fund	1178–1190	1150 sh	1150 s
1252 m	1255 vw	$2\nu_{23}$	1250–1260	1235 w	
1276 s	1282 s	A_1-fund	1270–1290	1260 m	1270 s
1296 vw		$\nu_{11} + \nu_{23}$			
1340 sh	1340 w	$2\nu_{11}$	1310–1350		
1383 s	1380 s	A_1-fund	1370–1395	1358 s	1360 s
1417 s	1416 m	A_1-fund	1410–1440	1396 s	1407 s
1438 w	1435 vw	$\nu_{11} + \nu_{22}$			
1448 w	1450 vw				
1500 s	1500 w	B_1-fund	1485–1500	1470 s	
1524 m	1520 vw	$2\nu_{22}$	1510–1525	1525 m	
1720 m		$\nu_{10} + \nu_{21}$		1720 m	
1760 m		$2\nu_{21}$		1770 m	
3110 m	3106 m	$A_1 + B_1$-fund	3100–3110	2900	
3125 m	3126 s	A_1-fund	3120–3130	3070 vs 3140	

The observed infrared and Raman data are given in Tables I–IV. The assignments of these vibrations are based on the following considerations. According to the assignments of unsubstituted five-membered rings, A_1 and B_1 vibrations are usually found at wavelengths higher than 900 cm^{-1} [3–8]. Raman spectra were recorded in order to be able to assign the A_1 modes, as these modes usually give rise to strong Raman absorptions. The high intensity of A_1 modes compared with modes of other symmetries is founded on theoretical grounds [7]. After the assignment of the A_1 vibrations, only B_1 modes and combination bands remain in the 1600–900 cm^{-1} region. A large number of overtones and combination bands appear in the infrared spectra, especially in the 2000–3000 cm^{-1} region. Below we list only the overtones and combination bands which are important for the assignments.

Overtones and Combination Bands

$Zn(Pz)_2$ $2\nu_{21} = 1772\ cm^{-1}$; obs. $1760\ cm^{-1}$
$\nu_{10} + \nu_{21} = 1729\ cm^{-1}$; obs. $1720\ cm^{-1}$
$2\nu_{22} = 1520\ cm^{-1}$; obs. $1524\ cm^{-1}$
$\nu_{11} + \nu_{22} = 1430\ cm^{-1}$; obs. $1438\ cm^{-1}$
$1450\ cm^{-1}$; obs. $1448\ cm^{-1}$
$2\nu_{11} = 1340\ cm^{-1}$; obs. $1340\ cm^{-1}$
$\nu_{23} + \nu_{11} = 1298\ cm^{-1}$; obs. $1296\ cm^{-1}$
$2\nu_{23} = 1256\ cm^{-1}$; obs. $1252\ cm^{-1}$

The bands at 1524, 1450, 1435, 1340 and 1252 cm^{-1} are also found – with very low intensity – in the Raman spectrum.

$Zn(ClPz)_2$ $2\nu_{21} = 1670\ cm^{-1}$; obs. $1662\ cm^{-1}$
$2\nu_{11} = 1336\ cm^{-1}$; obs. $1333\ cm^{-1}$
$2\nu_{22} = 1226\ cm^{-1}$; obs. $1226\ cm^{-1}$
$2\nu_{21} - \nu_{11} = 1002\ cm^{-1}$; obs. $1002\ cm^{-1}$

The bands at about 1333 and 1226 cm^{-1} are observed as weak bands in the Raman spectrum. The remaining absorptions between 900 and 1600 cm^{-1} are assigned as B_1 fundamentals. The difference between the A_2 and B_2 modes in the 600–900 cm^{-1} region is easily made as the A_2 species are inactive in the infrared spectrum. Below 600 cm^{-1} only metal–ligand vibrations are expected in salts of HPz.

TABLE II. Observed Infrared and Raman Bands in $Zn(ClPz)_2$ and HClPz.

$Zn(ClPz)_2$				HClPz	
IR	Raman	Assignment $Zn(ClPz)_2$	IR range in other salts	IR	Raman
	200 s	A_1-fund			
250 s		B_1-fund	200–515		120 m
290 s	286 s	A_1-fund	200–515		271 m
336 s	330 s	B_1-fund	310–375	296 m	300 m
390 m	390 vw	$2\nu_9$		{473	320 w
515 m	518 m	A_1-fund	420–525	{479 s	488 vs
613 s	618 vw	B_2-fund	610–622	609 s	610 w
668 vw	670 m	A_2-fund	668–680	645 w	648 w
770 vw		A_2-fund	760–770	810sh/798 s	795 w
835 s	830 w	B_2-fund	830–840	850 s	
945 m	948 m	B_1-fund	935–960	942 s	940 m
960 s}	972 vs	A_1-fund	960–980	955 sh	952 m
968 s}				972 s	968 s
1002 s	1007 vvw	$2\nu_{21} - \nu_{11}$	980–1002		
1059 s	1060 m	B_1-fund	1050–1076	1035 s	1043 s
1153 s	1150 m	B_1-fund	1150–1162	1141 s	1143 m
1207 s	1212 s	A_1-fund	1190–1230	1198 s	1200 s
1226 m	1221 sh	$2\nu_{22}$	1220–1240	{1220 w	
				{1250 m	
1300 s	1307 vs	A_1-fund	1285–1311	1290 m	1285 s
1333 m	1336 m	$2\nu_{11}$	1333–1350		
1370 s	1366 s	A_1-fund	1370–1390	1340 s	1344 m
1390 s	1392 s	A_1-fund	1390–1402	1378 s	1383 vs
1527 w	1525 w	B_1-fund	1515–1527	1565 m	1566 w
1662 s		$2\nu_{21}$	1660–1665	1501 m	
3120 s	3120 s	$A_1 + B_1$-fund	3120–3140	2900	
				3080 vs	
				3140	

TABLE III. Observed Infrared and Raman Bands in $Zn(BrPz)_2$ and HBrPz.

$Zn(BrPz)_2$				HBrPz	
IR	Raman	Assignment $Zn(BrPz)_2$	IR range in other salts	IR	Raman
	150 m				94 sh
224 m	230 m	A_1-fund			110 s
250 s	250 m	B_1-fund	200–508		220 w
270 s	260 ms	A_1-fund	200–508		242}vs
311 s	300 s	B_1-fund	291–362	254 m	254}
420 s	420 m	A_1-fund	335–410	362 m	372 vs
614 s	612 vw	B_2-fund	610–620	605 s	
670 vw	663 m	A_2-fund	670–680	642 w	646 w
		A_2-fund	750–760	800 s	805 vw?
840}s	830}w	B_2-fund	830–845	810 sh	
843}	840}			850 s	860 w?
					914 w
939 s	940 sh	B_1-fund	940–945	940 s	930 sh
945 s	955 s	A_1-fund	945–970	952 s	944 s
1005 m	1005 vw	$2\nu_{21} - \nu_{11}$	990–1010		
1061 s	1065 w	B_1-fund	1050–1070	1035 s	1039 s

(continued overleaf)

TABLE III *(continued)*

$Zn(BrPz)_2$				HBrPz	
IR	Raman	Assignment $Zn(BrPz)_2$	IR range in other salts	IR	Raman
1160 m	1150 w	B_1-fund	1150–1162	1142 s	1140 m
1198 m	1200 s	A_1-fund	1190–1220	1188 s	1189 s
1223 w		$2\nu_{22}$	1220–1230	1210 w	
				1245 w	
1292 s	1295 s	A_1-fund	1280–1302	1278 m	1274 s
1332 w	1334 w	$2\nu_{11}$	1325–1335	1290 w	
1368 m	1360 m	A_1-fund	1360–1380	1335 s	1336 s
1382 s	1382 s	A_1-fund	1375–1395	1375 s	1378 vs
1512 w	1510 vw	B_1-fund	1490–1512	1493 m	
1670 s		$2\nu_{21}$	1650–1670	1566 m	1546 w
				1650 s,br	
3115 s	3118 m	$A_1 + B_1$-fund	3115–3140	2900	
				3070 vs	
				3120	

TABLE IV. Observed Infrared and Raman Bands in $Zn(IPz)_2$ and HIPz.

$Zn(IPz)_2$			HIPz	
IR	Assignment $Zn(IPz)_2$	IR range in other salts	IR	Raman
				65 m
195 w				82 sh
230 s	$A_1 + B_1$-fund	180–490		113 s
260 s	A_1-fund	180–502		145 m
300 s	B_1-fund	270–346	220 w	218 m
				228 sh
				243 m
				301 m
390 s	A_1-fund	322–410	320 m	319 vs
614 s	B_2-fund	610–620	610 s	608 w
670 vw	A_2-fund	660–670	649 m	651 w
	A_2-fund	770–780	810 vs	
840 vs	B_2-fund	830–850	870 s	
935 sh	B_1-fund	940–950	940 s	910 m
946 s	A_1-fund		952 s	940 s
1002 s	$2\nu_{21} - \nu_{11}$	990–1005		
1060 vs	B_1-fund	1040–1072	1035 s	1040 m
1159 s	B_1-fund	1159–1165	1142 s	1143 m
1190 s	A_1-fund	1160–1205	1178 m	1178 s
1228 m	$2\nu_{22}$	1228–1230	1218 w	
			1260 sh	
1287 s	A_1-fund	1282–1295	1269 m	1263 s
1335 w	$2\nu_{11}$		1298 w	
1380 sh	A_1-fund	1370–1385	1320 s	1320 m
1372 s	A_1-fund	1370–1380	1328 s 1360 s	1365 vs
			1450 w	
			1475 m	
1493 m	B_1-fund	1490–1510	1537 s	1540 w
1505 sh		1500–1510	2900	
1680 m	$2\nu_{21}$		3040 vs	
3100 sh 3110 m	$A_1 + B_1$-fund		3120	

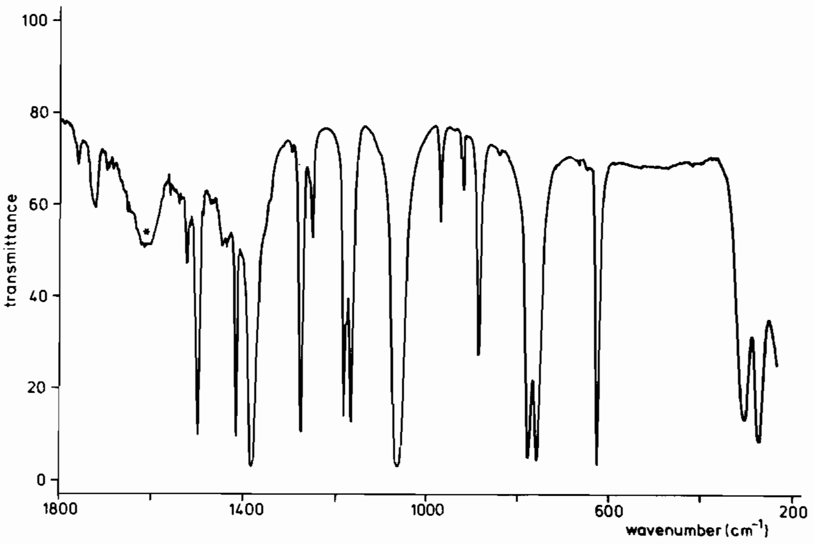


Fig. 1a. Infrared spectrum in the 200–1800 cm^{-1} region of Zn(Pz)$_2$. The band with an asterisk is due to water in the used CsI.

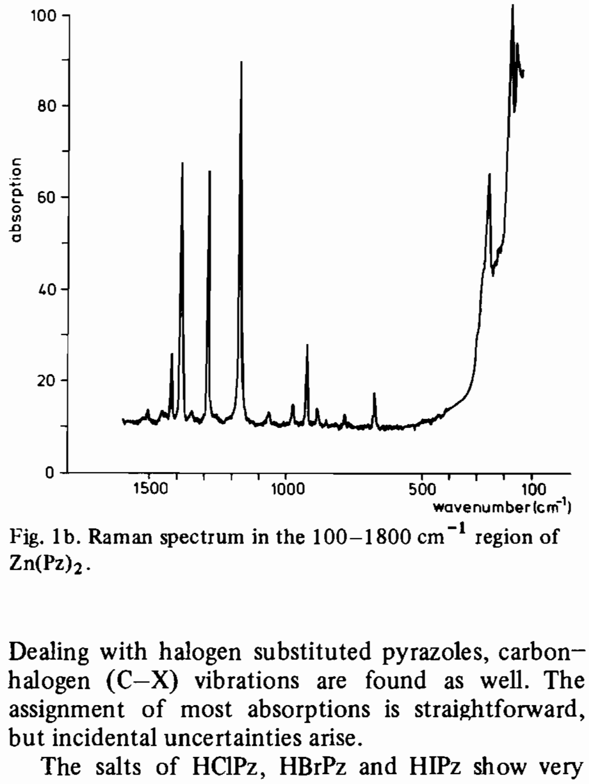


Fig. 1b. Raman spectrum in the 100–1800 cm^{-1} region of Zn(Pz)$_2$.

Dealing with halogen substituted pyrazoles, carbon–halogen (C–X) vibrations are found as well. The assignment of most absorptions is straightforward, but incidental uncertainties arise.

The salts of HClPz, HBrPz and HIPz show very similar vibration spectra. Differences are found only in the positions of the C–X vibrations. Therefore, only the assignment of Zn(ClPz)$_2$ will be discussed together with that of Zn(Pz)$_2$. In the Raman and infrared spectra of Zn(Pz)$_2$ only two instead of three C–H stretch vibrations are observed at about 3000 cm^{-1}. The strong Raman bands at respectively 3126 and 3106 cm^{-1} are assigned to the expected A$_1$ modes. The B$_1$ mode probably overlaps one of the A$_1$ modes. Some other bands possibly also overlap, especially in the Raman spectrum. Two B$_1$ modes assigned to the infrared bands at 1064 and 1075 cm^{-1} probably coincide at 1060 cm^{-1} in the Raman spectrum. Another B$_1$ mode assigned to the infrared absorption at 1182 cm^{-1} probably overlaps with the strong A$_1$ mode at 1168 cm^{-1} in the Raman spectrum. Vibrations associated with the metal–ligand bond expected at wavelengths below 200 cm^{-1} are not observed.

In the case of Zn(ClPz)$_2$ only one C–H stretch vibration is observed at about 3000 cm^{-1}. This vibration which appears as a strong band in the Raman spectrum is assigned to the A$_1$ mode. The B$_1$ mode probably overlaps with the A$_1$ vibration.

The band at 670 cm^{-1} is assigned to the A$_2$ ring vibration. The A$_2$ C–H vibration is not observed. A very weak band at 770 cm^{-1} found in some other salts might be due to this A$_2$ mode. It is also possible that the A$_2$ vibration overlaps with the B$_2$ vibration at about 830 cm^{-1}. In transition metal complexes of the neutral ligands two absorptions are observed at about 840 and 830 cm^{-1} which might be an argument for the last possibility [6].

Description of the Vibrations of Salts and Neutral Ligands

As reported by Zecchina *et al.* [3] 18 normal modes can be expected for a pyrazolato ion. These are classified as 13 in-plane and 5 out-of-plane vibration modes. The in-plane vibrations can be described as: three C–H stretching, four ring stretching, two in-plane ring, one ring breathing and three in-plane C–H bending vibrations. The five out-of-plane modes include three out-of plane C–H bending and two out-of-plane ring vibrations. This classification of vibra-

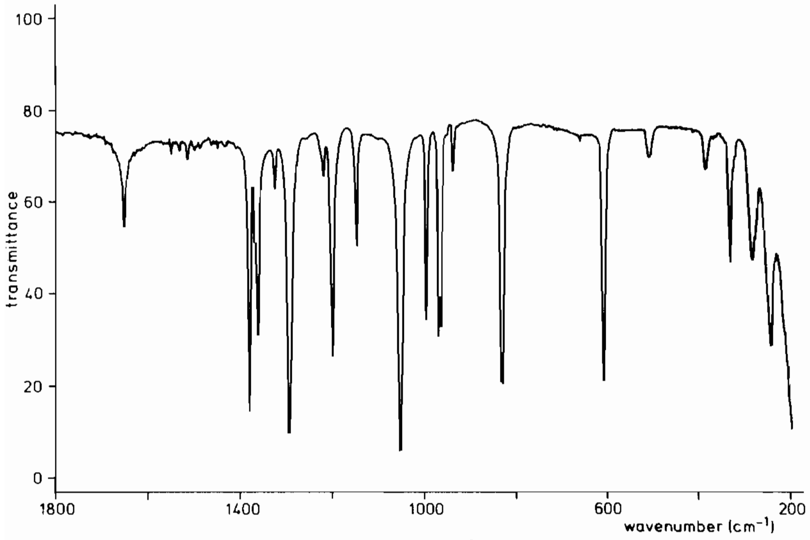


Fig. 2a. Infrared spectrum in the 200–1800 cm^{-1} region of $Zn(ClPz)_2$.

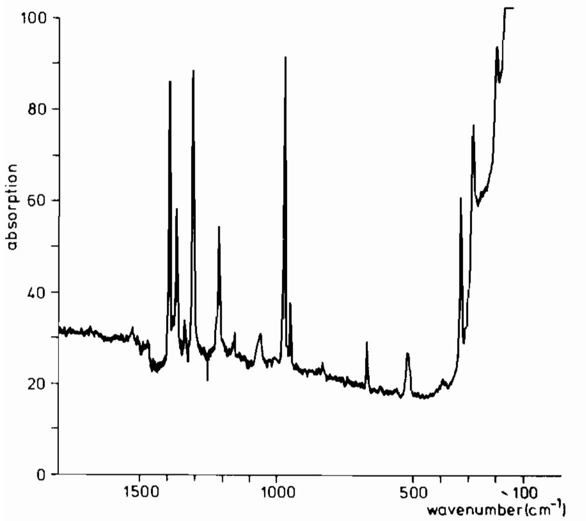


Fig. 2b. Raman spectrum in the 100–1800 cm^{-1} region of $Zn(ClPz)_2$.

tions is used for the description of the salts. The range in which the different fundamentals are usually found, is obtained from assignments of other five-membered rings like 1,3,4-oxadiazole [8, 9] and 1,2,4-triazole [10], whereas the existing assignments of the neutral ligands are also used. Normal coordinate analyses of pyrazole [5] and 1,2,4-triazole [10] show that a strong mixing of vibrations occurs, especially in the region between 1300 and 1100 cm^{-1}. Therefore, we described the absorption bands in this region as mixed fundamentals. Below 600 cm^{-1}, mixing of vibrations occurs also in the salts of the halogen substituted pyrazoles [2]. The C–X stretching (A_1) mode couples with the M–N stretching (A_1) and the C–X in-plane bending (B_1) with the M–N stretching (B_1) vibration. Coupling between the in-plane M–N bending (B_1) vibration and the in-plane C–X bending (B_1) vibration is possible, also for symmetry reasons.

With the information obtained from the salts, assignments of the neutral ligands are given. The spectra of the salts are easier to interpret because of the absence of N–H vibrations and a higher C_{2v} symmetry. Vibrations of salts and neutral ligands are observed in the same regions and therefore a comparison seems realistic.

Our assignment of HPz is in agreement with the assignment based on a normal coordinate analysis of Troitskaya [5]. Our assignments of HClPz and HBrPz are different from the assignments given by Reedijk *et al.* [2, 6]. Especially the vibrations associated with the C–X bond are different, whereas also a number of absorptions in the 1300–1100 cm^{-1} region are assigned differently.

The assignment of HIPz is based partly on the assignments of the other ligands, as no Raman spectrum of $Zn(IPz)_2$ was available. A number of lines in the assignments of HIPz and the salts of HIPz might therefore be interchanged. These bands are marked in Table V and VI with an asterisk.

Acknowledgments

The authors are indebted to Dr. W. L. Driessen and Dr. J. G. Haasnoot for their interest in this study and to Dr. M. W. G. de Bolster for recording the Raman spectra.

TABLE V. Description of the Observed Normal Vibrations in the Metal Salts.

Sym.	ν No.	$Zn(Pz)_2$	ν No.	$Zn(ClPz)_2$	$Zn(BrPz)_2$	$Zn(IPz)_2$	Description
A_1	1	3126					νC–H
	2	3110	1	3120	3115	3100	νC–H
	3	1417	2	1390	1382	1372	νring
	4	1383	3	1370	1368		νring
	5	1276	4	1300	1272	1287	βC–H + ring
	6	1167	5	1207	1198	1190	ring + βC–H
	7	922	6	968	945	946*	ring
			7	515	420	390	νC–X + νM–N
	8	270	8	290	270	260*	νM–N + (νC–X)
	9	180	9	200 (R)	224	230?	βM–N + (νC–X)
A_2	10	843	10				γC–H
	11	670	11	668	670	670	ring
	12		12				γM–N
B_1	13	3110	13	3120	3115	3100	νC–H
	14	1500	14	1527	1512	1493	νring
	15	1182	15	1153	1160	1159	ring + βC–H
	16	1075					βC–H
	17	1064	16	1059	1061	1060	βC–H
	18	972	17	954	939	935*	ring
			18	336	311	300	βC–X + νM–N
	19	300	19	250	250	230*	νM–N + (βC–X)
	20		20				βM–N + (βC–X)
B_2	21	886	21	835	840	841	γC–H
	22	780					γC–H
	23	628	22	613	614	614	ring
	24		23				γM–N + (γC–X)
			24				γC–X + γM–N

TABLE VI. Description of the Observed Normal Vibrations in the Solid Neutral Ligands.

Sym.	HPz	HClPz	HBrPz	HIPz	Description
A′	3140	3120	3120	3120	νC–H
	3074	3085	3070	3040	νC–H
	3070				νC–H
	2900	2900	2900	2900	νN–H
	1470	1565	1562	1536	ring + βN–H
	1396	1378	1372	1365	ring + βN–H
	1358	1340	1335	1328	ring + βN–H
	1258	1290	1278	1268	βC–H + ring + βN–H
	1152	1196	1186	1178	ring + βC–H + βN–H
	1137	1141	1140	1142	ring + βC–H + βN–H
	1060				βC–H
	1035	1035	1033	1031	βC–H
	938	972	950	955	ring
	926/918	940	938	938	ring
		480/473	361	321	νC–X
		300	254	220 (R)	βC–X

(continued overleaf)

TABLE VI. *(Continued)*

Sym.	HPz	HClPz	HBrPz	HIPz	Description
A″	894/880				γC–H + γN–H
	841	850	850	860	γC–H + γN–H
	765	810	810	810	γC–H + γN–H
		798	800		γN–H + γC–H
	655	643	642	658	ring + γN–H
				650	
	618	609	605	610	ring + γN–H
		120 (R)	110 (R)	113 (R)	γC–X

References

1 Part I. J. G. Vos and W. L. Groeneveld, *Inorg. Chim. Acta, 24,* 123 (1977).

2 Part II. J. G. Vos and W. L. Groeneveld, *Inorg. Chim. Acta, 26,* 73 (1978).

3 A. Zecchina, L. Cerruti, S. Coluccia and E. Borello, *J. Chem. Soc. B,* 1363 (1967).

4 J. Reedijk, *Rec. Trav. Chim., 88,* 1451 (1969).

5 V. S. Troitskaya, N. D. Konevskaya, V. G. Vinokurov and V. I. Tyulin, *Khim. Geterotsikl. Soedin, 10,* 542 (1974).

6 J. Reedijk, J. C. A. Windhorst, N. H. M. van Ham and W. L. Groeneveld, *Rec. Trav. Chim., 90,* 234 (1971).

7 E. B. Wilson, Jr., J. C. Decius and C. Cross, "Molecular Vibrations", McGraw–Hill, New York (1955).

8 D. H. Christensen, J. T. Nielsen and O. F. Nielsen, *J. Mol. Spectry., 24,* 225 (1967).

9 D. H. Christensen, J. T. Nielsen and O. F. Nielsen, *J. Mol. Spectry., 25,* 197 (1968).

10 D Bougeard, N. le Calvé, B. Saint Roch and A. Novak, *J. Chem. Phys., 64,* 5152 (1976).