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Pyrazolato and Related Anions.
Part II [1]. Salts of Halogeno Pyrazoles

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A number of metal salts of 4-chloropyrazole, 4-bromopyrazole and 4-iodopyrazole is reported. Cd, Zn, Ni, Cu and Co(III) salts are synthesized from an aqueous ammonia solution, Co(II) salts by addition of NaOH to a solution of the 4-halogenopyrazole solvated Co(II) salts in water.

The compounds are characterized and identified by chemical analyses, infrared spectra and ligand-field spectra. The pyrazolato ion acts as a bidentate ligand in all cases. In the Cd and Ni compounds extra ligands as NH_3 are involved and a pseudo-octahedral symmetry is found for the coordination. Tetrahedral and square-planar surroundings are found in the other salts of divalent metals. In the far-infrared spectra, strong couplings between the C–halogen and the metal–ligand vibrations have been observed, caused by the symmetry of the bridging anions.

Introduction

The first paper in this series dealt with the preparation and characterization of metal salts of pyrazole (HPz). It seemed interesting to investigate the salts of substituted pyrazolato ions to see if there is any relation between the pK_{base} of the neutral ligands and the obtained products in comparison with HPz, pK_b being 2.52. Alkyl substituted pyrazoles have a higher pK_b, *e.g.* the pK_b of 4-methylpyrazole is 3.09 [2]. When electrophilic groups are substituted in the five-membered ring the pK_b becomes lower. The pK_b's of 4-iodopyrazole (HIPz), 4-bromopyrazole (HBrPz) and 4-chloropyrazole (HClPz) are, respectively, 0.80, 0.64 and 0.60 [2]. According to Reedijk *et al.* [3] the pK_b is a measure for the strength of the neutral ligand in transition metal complexes. In this paper the preparation and characterization of metal salts of the anions IPz^-, $BrPz^-$ and $ClPz^-$ are reported. Physical measurements have been carried out in order to obtain information on the bonding and structure in the obtained compounds.

Experimental

Commercially available pyrazole and metal salts were used without further purification. 4-Chloropyrazole was synthesized as described by Huttel [4]; 4-bromopyrazole and 4-iodopyrazole were prepared as described by Buchner and Fritsch [5].

The procedure for the preparation of the pyrazolato salts has been described in Part I of this series. Because of the solubility of a number of the salts in ethyl alcohol and diethyl ether the precipitated products were washed only with water and dried *in vacuo.*

It was not always possible to obtain the pyrazolato salts by addition of NaOH to a complex of the neutral ligand, *e.g.* on addition of two mol NaOH to one mol $Ni(HBrPz)_4Cl_2$ in water, a compound $Ni(BrPz)Cl(HBrPz)_2$ was formed. With an excess of hydroxide (4:1) in alcohol a yellow solution of the Ni salt was formed, but a precipitate could not be isolated. Starting from neutral ligand complexes, neither could the copper complexes be obtained sufficiently pure.

The obtained compounds are listed in Table I. The Cd and Ni salts contained water and ammonia after being dried at room temperature. These extra ligands could be removed by heating at 200 °C. The copper salts with the anions $ClPz^-$ and $BrPz^-$ contained strongly bonded water; in the corresponding IPz^- salt, on the other hand, the water is easily removed on drying at room temperature. The rest of the compound is obtained pure after drying *in vacuo* at room temperature.

The cobalt salts have been obtained after addition of NaOH to the complexes of the neutral ligand in water. They are very sensitive to oxygen in the presence of water, so a nitrogen atmosphere was required.

The compound $Ni(BrPz)_2(pyridine)_2 \cdot H_2O$ has been obtained by dissolving $Ni(BrPz)_2(NH_3)_2 \cdot H_2O$ in ethyl alcohol in the presence of an excess of pyridine. The precipitate was washed with diethyl ether and dried *in vacuo.*

TABLE I. Analytical Data and Colours of the Pyrazolato Salts[a].

Compounds	Metal %	C %	H %	N %	Hal. %	Colour
$Cd(IPz)_2$	22.5	14.53	0.81	11.20	49.99	White
	(22.55)	(14.46)	(0.81)	(11.24)	(50.92)	
$Zn(IPz)_2$	14.52	16.13	1.02	12.27	55.39	White
	(14.48)	(15.97)	(0.89)	(12.41)	(56.22)	
$Co(IPz)_2$	12.83					Purple
	(13.24)					
$Ni(IPz)_2$	12.56	16.35	1.22	12.75		Orange
	(13.20)	(16.19)	(0.90)	(12.50)		
$Cu(IPz)2$	14.58	16.46	1.17	12.18	55.20	Yellow
	(14.13)	(16.03)	(0.90)	(12.46)	(56.46)	
$Co(IPz)_3$	9.96					Orange
	(9.23)					
$Cd(BrPz)_2$	26.8	17.87	1.13	13.49	38.91	White
	(27.79)	(17.82)	(1.00)	(13.86)	(39.51)	
$Zn(BrPz)_2$	18.16	20.20	1.23	15.59	44.69	White
	(18.29)	(20.17)	(1.12)	(15.68)	(44.72)	
$Co(BrPz)_2$	16.2					Purple
	(16.79)					
$Ni(BrPz)_2$	15.71	20.77	1.41	15.57		Orange
	(16.73)	(20.55)	(1.14)	(15.97)		
$Cu(BrPz)_2 \cdot H_2O$[b]	17.16	19.39	1.78	15.04	42.55	Purple–Grey
	(17.01)	(19.29)	(1.62)	(15.00)	(42.78)	
$Co(BrPz)_3$	11.54					Orange
	(11.87)					
$Cd(ClPz)_2$	34.5					White
	(35.6)					
$Zn(ClPz)_2$	24.2					White
	(24.34)					
$Co(ClPz)_2$	21.7					Purple
	(22.50)					
$Ni(ClPz)_2$	21.7	26.16	1.79	20.80		Orange
	(22.42)	(27.51)	(1.52)	(21.38)		
$Cu(ClPz)_2 \cdot 2H_2O$	21.3	23.38	2.69	20.05		Purple–Grey
	(20.98)	(23.80)	(2.64)	(18.49)		
$Co(ClPz)_3$	15.70					Orange
	(16.20)					
$Cd(BrPz)_2(NH_3)_2 \cdot 2H_2O$	24.1					White
	(23.7)					
$Ni(IPz)_2(NH_3)_2 \cdot 2H_2O$	11.6					Purple
	(11.41)					
$Ni(BrPz)_2(NH_3)_2 \cdot 2H_2O$	14.06					Purple
	(13.98)					
$Ni(BrPz)_2(py)_2 \cdot H_2O$[c]	11.16					Light Blue
	(11.14)					
$Ni(ClPz)_2(NH_3)_2 \cdot 2H_2O$	18.0					Purple
	(17.69)					
$Cu(IPz)_2 \cdot 2H_2O$	13.23					Purple
	(13.09)					

[a] Calculated values in parentheses. [b] Oxygen, found 4.22%, calculated 4.28%. [c] py = pyridine.

Physical Measurements and Analyses

Thermal analytical measurements were carried out by Mr. W. Crama on a Mettler Vacuum Thermal Analyzer, TA1.

Diffuse reflectance spectra were obtained in a Beckman DK-2A ratio recording spectrophotometer with MgO as a reference. Infrared spectra were recorded on a Perkin Elmer 580 infrared spectrophotometer (4000–180 cm^{-1}), as nujoll mulls and CsI pellets.

Metal analyses were carried out by complexometric titrations after prior decomposition by heating in nitric acid. Carbon, hydrogen, carbon and halogen analyses were carried out by the Microanalytical

TABLE II. Far-infrared Data (cm^{-1}).[a]

Compounds	ν C–X	β C–X	ν M–N
HIPz	318	220?	–
$Cd(IPz)_2$	360	270	<200
$Zn(IPz)_2$	405(sh), 390	300	260, 230
$Co(IPz)_2$	410	310	265, 245
$Ni(IPz)_2$	322	–	495, 458
$Ni(IPz)_2(NH_3)_2 \cdot 2H_2O$	362	272	336, 320 (M–NH_3)
$Cu(IPz)_2$	410	346	290, 265
$Co(IPz)_3$	362	290, 278	502, 490
HBrPz	361	254	
$Cd(BrPz)_2$	410	291, 276	<200
$Zn(BrPz)_2$	420	311	262, 242
$Co(BrPz)_2$	437	320	270, broad
$Ni(BrPz)_2$	335	–	512, 460
$Ni(BrPz)_2(NH_3)_2 \cdot 2H_2O$	400	275	346, 320 (M–NH_3)
$Ni(BrPz)_2(py)_2 \cdot H_2O$	430, 405	275	345, 290 (M–py)
$Cu(BrPz)_2 \cdot H_2O$	442	362	300, 280
$Co(BrPz)_3$	383 w	308, 300	508
HClPz	477, 470	296	
$Cd(ClPz)_2$	505	310	<200 265?
$Zn(ClPz)_2$	513	335	282, 245
$Co(ClPz)_2$	512	342	295, 275
$Ni(ClPz)_2$	–	346	460, 382
$Ni(ClPz)_2(NH_3)_2 \cdot 2H_2O$	520?	295	363, 344 (M–NH_3)
$Cu(ClPz)_2 \cdot 2H_2O$	525	375	338, 328, 298
$Co(ClPz)_3$	420	320	512

[a] All bands are strong except for the C–Cl stretch, which is rather weak.

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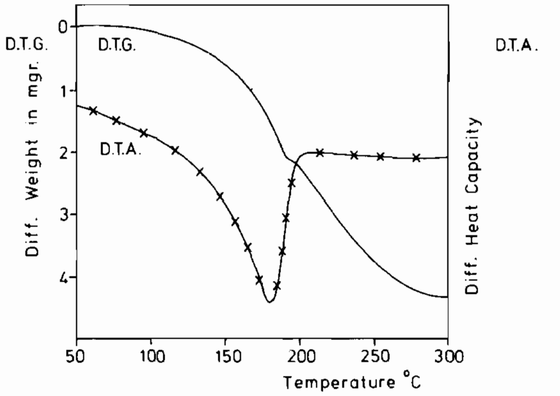

Figure 1. DTG and DTA curves of $Ni(BrPz)_2(NH_3)_2 \cdot 2H_2O$.

Results and Discussion

Thermoanalytical Experiments

$Ni(BrPz)_2 \cdot (NH_3)_2 \cdot 2H_2O$ has been used for thermoanalytical experiments. 255 mg of this compound was heated to 300 °C at a rate of 8 °C/min, under N_2 atmosphere. The D.T.G. and D.T.A. curves are given in Fig. 1. A decrease in weight of 43 mg or 16.9% is in agreement with a loss of 2 NH_3 + $2H_2O$. At 180 °C the D.T.A. curve shows a strong peak which halfway together with a change in the slope of the D.T.G. curve may indicate a change in coordination from octahedral to square-planar, caused by the loss of $2NH_3$. So we think that first two NH_3 molecules are removed and later the water. This is in agreement with the fact that the resulting orange compound, if not dried long enough, contains water and never NH_3.

Infrared Spectra

The overall picture of the IR spectra of the compounds in this paper is the same as for the salts in Part I. Two out-of-plane vibrations of the coordinated anion are IR inactive. So a C_{2v} symmetry for the anions is very likely and we may assume the pyrazolato group to be bidentate with the formation of a chain structure. A complete IR assignment of the salts will be published shortly. The OH-stretch vibrations in the copper compounds are found at 3555 cm^{-1} and at 3612 cm^{-1}, a sharp OH-bending is found at 1610 cm^{-1}. About the same values are found for $Cu(Pz)_2 \cdot H_2O$ [1]. No clear M–O vibrations could be assigned. The OH vibrations in the Cd and Ni salts are found in the same region, but not sharp and rather weak. In these Cd and Ni salts that are only

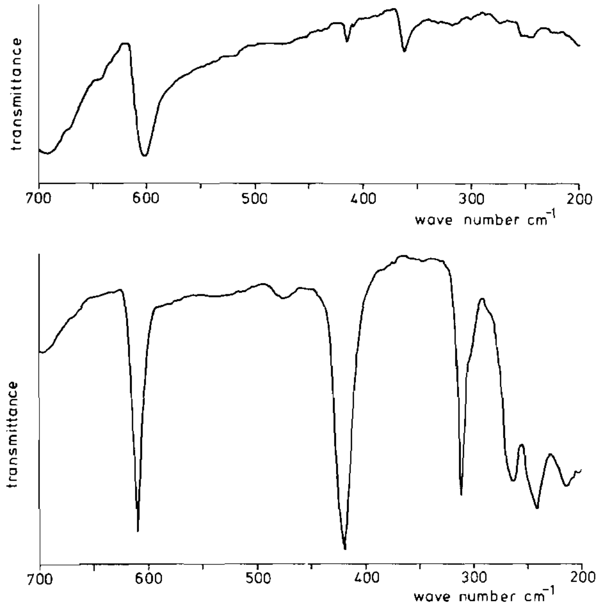

Figure 2. a) Far-infrared spectrum of solid HBrPz. b) Far-infrared spectrum of Zn(BrPz)$_2$.

dried at room temperature, NH$_3$ vibrations are found in the spectra as well: NH stretch vibrations at 3280 cm^{-1} and at 3375 cm^{-1}, a NH bending at 1600 cm^{-1}. A NH$_3$ symmetric deformation band is found at 1180 cm^{-1} and the NH$_3$ rocking at 560 cm^{-1}. All these frequencies make a coordination of the NH$_3$ most likely, a coordination that we expect to be rather weak according to the low rocking frequency [6].

Far-infrared Spectra

Far-infrared spectra were recorded in order to obtain information about the metal–ligand bond. The observed bands between 600 and 200 cm^{-1} are listed in Table II.

In the free ligand we find below 600 cm^{-1} vibrations associated with the C–halogen bond. A tentative assignment of these C–X bands is given below. We do not follow the assignment of Reedijk for HClPz and HBrPz, but compare our spectra with those of halogen substituted benzene derivatives [7].

In the spectra of the salts usually four bands are found (see Fig. 2 a, b), one sharp band at about 400 cm^{-1} and three near 300 cm^{-1}. All these bands are metal dependent. We assigned the first band to a C–X stretch vibration, the highest and sharpest band at 300 cm^{-1} as a C–X deformation and the other two as M–N bands. The high shifts of the ligand bands can be explained taking into account the symmetry of the five-membered ring. As for the infrared spectra we have concluded that the anion has C_{2v} symmetry and, therefore, acts as a bidentate. In this structure* we expect two M–N stretch vibrations with A_1 and B_1 symmetry. Of the two C–X vibrations mentioned above the C–X stretch has A_1 and the C–X deformation has B_1 symmetry. So a coupling of the vibrations with the same symmetry is obvious and when they are close enough, high shifts are expected. Similar high shifts as observed here have been found by Knetsch with complexes of diols [18]. A very clear example of this coupling is found for the orange Ni salts. In these square-planar complexes we find two M–N bands. One band fairly constant at 460 cm^{-1} and another at 385 cm^{-1} for the Ni(ClPz)$_2$ salt and at 512 cm^{-1} for the Ni(BrPz)$_2$ salt. We assigned the band at 460 cm^{-1} as a B_1 vibration because we think this band to be coupled with the reasonably constant C–X deformation. Then, the other band has A_1 symmetry and coupling with the very variable C–X stretch explains its changing place in the spectra.

The compound Ni(BrPz)$_2$(pyridine)$_2$·H$_2$O has been used in order to assign the far-infrared spectra of the purple Ni compounds. By replacing the NH$_3$ molecules of these salts by pyridine, it was possible to find the IR-bands associated with the NH$_3$ group. In these mixed compounds no coupling between the C–X and M–N vibrations is observed. This may be caused by hydrogen bonding between the water molecules and the halogens. Because of the strong coupling between the M–N and C–X bands it is not possible to conclude anything from the place of these bands. Nothing can be said about the influence of the pK_b of the ligand on the M–N frequency. Also a possible shift of the C–X vibrations in the anion when compared with the neutral ligand is obscured by the coupling effect, although in the square-planar Ni salts and the Co(III) salts a shift to higher wavelength is found.

Ligand-field Spectra

Ligand-field spectra have been recorded in order to obtain information about the coordination around

	HClPz	HBrPz	HIPz	C_6H_5Cl	C_6H_5Br	C_6H_5I
C–X stretch	477	361	318	415	314	266
C–X bending	296	254	220	297	254	220

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*We take the y-axis perpendicular to the molecular plane.

TABLE III. Ligand Field Spectra. Absorption Bands in kK, Calculated Dq and B Values in cm^{-1}.

Compounds	Absorption Bands			Calculated Parameters			
		$^4T_1(F) \leftarrow {}^4A_2$	$^4T_1(P) \leftarrow {}^4A_2$	Dq	B	Dq/B	β
$Co(ClPz)_2$		8.85	18.87	512	816	0.63	0.84
$Co(BrPz)_2$		8.55	18.87	515	797	0.65	0.82
$Co(IPz)_2$		8.85	17.85	512	756	0.67	0.77
$Co(Pz)_2$		8.8	17.5	500	750	0.67	0.77
	$^3T_{2g} \leftarrow {}^3A_{2g}$	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$				
$Ni(ClPz)_2(NH_3)_2 \cdot 2H_2O$	11.4	17.7	28.0	1140	765	1.49	0.74
$Ni(BrPz)_2(NH_3)_2 \cdot 2H_2O$	11.4	17.7	28.0	1140	765	1.49	0.74
$Ni(IPz)_2(NH_3)_3 \cdot 2H_2O$	11.4	17.7	28.0	1140	765	1.49	0.74
	$^1B_{1g} \leftarrow {}^1A_{1g}$						
$Ni(ClPz)_2$	21.05						
$Ni(BrPz)_2$	21.05						
$Ni(IPz)_2$	21.5						
$Ni(Pz)_2$	22.2						
$Cu(ClPz)_2 \cdot 2H_2O$	15.9 (sh) 19.6						
$Cu(BrPz)_2 \cdot H_2O$	18.2						
$Cu(IPz)_2$	–						
$Cu(IPz)_2 \cdot 2H_2O$	15.4 (sh) 19.2						
$Cu(Pz)_2 \cdot H_2O$	17.4						
	$^1T_{1g} \leftarrow {}^1A_{1g}$						
$Co(ClPz)_3$	20.8						
$Co(BrPz)_2$	20.8						
$Co(IPz)_3$	20.8						
$Co(Pz)_3$	20.0						

$\beta = B/B_o$

$B_o = 1030\ cm^{-1}\ (Ni^{2+})$, $B_o = 971\ cm^{-1}\ (Co^{2+})$ [11]

sh = shoulder

the metal ion. The observed bands and calculated values for Dq, B, Dq/B are listed in Table III. For comparison the values for unsubstituted pyrazolates are added. The metal ions in the Co(II) salts are coordinated tetrahedrally. The calculated Dq is about the same as for $Co(Pz)_2$ but the values for B are higher. So it seems that the substitution of halogens in the ring causes a change in B and not a change in Dq. B varies with the inductive effect of the halogen atoms, which also decreases in the order Cl > Br > I.

The ligand field spectra of the Co(III) salts are in agreement with a low spin octahedral coordinated metal ion. Like in the Co(II) salts, no influence of the pK_b on the Dq is observed. The $^1T_{1g} \leftarrow {}^1A_{1g}$ transition shifts with lower pK_b to higher wavelength, which is possibly explained by a higher value for F_4. So here also the influence of the pK_b of the neutral ligand seems to be found in the nephelauxetic effect.

Information about the coordination in the Zn and Cd compounds can be obtained by using Co(II) dopes. As in $Zn(XPz)_2$ the Zn salts showed tetrahedral surrounded Co(II) ions, so we suggest that the Zn compounds are tetrahedral complexes. No Co(II) dope in Cd could be obtained and this, with the fact that the Cd compounds contain extra ligands as the Ni salts, makes a tetrahedral coordination in the Cd salts unlikely.

The absorption band in the orange Ni salts is assigned as the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition, in a square-planar arrangement the compounds are diamagnetic. The absorption bands in the purple Ni salts correspond with octahedral surrounded Ni(II) ions. The calculated Dq value falls in the range for a Ni atom with six coordinating nitrogen atoms. This, together with the observed NH_3 vibrations in the IR spectra, makes coordination of two NH_3 molecules very likely. No influence of the pK_b of the ligands is found in the spectra. Differences in the anions are possibly masked by the presence of the NH_3 molecules. With the rule of average environment we obtain a Dq of about 1170 cm^{-1} for the coordinating anions. This is in reasonable agreement with the value for an octahedral surrounded Co(II) ion, 1150 cm^{-1}, which is calculated out of the tetrahedral Co(II) salts.

Dq and B of the Ni compounds were calculated using the method developed by Reedijk *et al.* [9]. In all copper compounds we suppose the anions to be bridging in the XY plane and the water, when present along the Z-axis. $Cu(BrPz)_2 \cdot H_2O$ shows a symmetric band at 18.2 kK, so we think that in this salt the water is bridging two copper atoms, like in $Cu(Pz)_2 \cdot H_2O$. Because of the rather broad and asymmetric bands of the other hydrated salts, such a structure is not expected there. The absorption bands of the yellow $Cu(IPz)_2$ fall in the charge transfer region, so probably the metal ions are square-planar coordinated.

When we compare the Ni and Cd salts of the halopyrazoles with the salts of the HPz, the most important difference is found in the extra coordinating NH_3 molecules. The reason for this is probably the size of the ligands. In the halopyrazoles being larger because of the C–X group, extra ligands can easily find a place in the lattice.

Conclusions

As a result of this investigation we can draw the following conclusions.

1) In all cases the anions are bidentate coordinated.

2) Influence of the pK_{base} of the ligands on the salts is not found in the Dq value, but possibly in the nephelauxetic effect.

3) Because of the strong coupling between the C–X and M–N bands nothing can be concluded from the place of the metal–ligand bands.

4) In the octahedral Ni and Cd salts ammonia molecules are coordinated to the metal ion.

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