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Pyrazolato and Related Anions. Part IV. Salts of 4-Nitropyrazole

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A number of metal salts of 4-nitropyrazole (HNO_2Pz) is reported. Salts of Cd, Zn, Mn, Co, Ni and Cu are synthesized from ammonia solution, or by addition of NaOH to a NHO_2Pz complex in water.

The compounds are identified and characterized by chemical analyses, infrared and ligand field spectra. The pyrazolato anion coordinates as a bidentate ligand. In the salts of Cd, Mn, Co, Ni, and Cu ammonia and water molecules are participating in the coordination of the metal ion. A tentative vibrational assignment of salts and neutral ligand is given.

Introduction

This paper is a part of our investigations on salts of pyrazoles. Earlier papers [1, 2] dealt with the preparation and characterization of salts of pyrazole (HPz), 4-chloropyrazole (HClPz), 4-bromopyrazole (HBrPz) and 4-iodopyrazole (HIPz).

Coordination complexes of neutral 4-nitropyrazole (HNO_2Pz) have been published and used for an assignment of the infrared spectrum of the HNO_2Pz ligand by Reedijk *et al.* [3]. The preparation and the far-infrared spectrum of $Ag(NO_2Pz)$ have been reported by Okkersen [4].

In the salts of HPz and HXPz a correlation between the pK_{base} of the neutral ligand and the spectra of the obtained products is not conclusive. The ligand field spectra give an indication of a reflex of the pK_{base} on the nephelauxetic effect, but a possible shift in metal–ligand vibrations in the far-infrared spectrum of halogenopyrazolates is obscured by an interaction between metal–ligand vibrations and carbon–halogen vibrations [2]. In HNO_2Pz these interacting ligand vibrations are absent and the low pK_{base} of HNO_2Pz (–1.96) may yield more information about the correlation between this pK_b and the ligand field spectra. So the salts of this pyrazole derivatives have been prepared and investigated. In this paper a tentative assignment of the salts has been given, mainly based on the infrared and Raman spectra of the zinc compound. This assignment has been used for the description of the infrared and Raman spectra of the neutral ligand.

Experimental

4-nitropyrazole was synthesized as described by Morgan [5]. Commercially available metal salts were used without further purification. To obtain the pyrazolato salts two procedures were followed:

1) a hydrated metal chloride was added to HNO_2Pz, both dissolved in 25% aqueous solution of ammonia.
2) addition of NaOH to a solution of a HNO_2Pz solvated metal complex in water.

In both cases the salts were obtained as precipitates, centrifugated, washed with water, ethyl alcohol and diethyl ether and finally dried *in vacuo* at room temperature (Table I, 1a, 2a). Compounds which contained water and ammonia were heated at 180 °C (Table I, 1b, 2b). No decomposition of the salts was found up to 250 °C. The Mn(II) and Co(II) salts appeared to be sensitive to oxygen and had to be prepared in N_2 atmosphere. The dry Mn(II) compound could be isolated but the Co(II) compound, obtained as a yellow powder from ammonia solution was oxidized very rapidly. We only succeeded in recording ligand field and infrared spectra of this compound, while no satisfactory analyses were obtained. These spectral data are given because of the importance of this compound in the present series. The information obtained from infrared and ligand field spectra is in agreement with the formula $Co(NO_2Pz)_2(NH_3)_2 \cdot xH_2O$.

1-D,4-nitropyrazole was prepared by refluxing of a solution of HNO_2Pz in D_2O.

From infrared intensity measurements the deuteration appeared to be completed for about 90%.

Physical Measurements and Analyses

Thermal analytical measurements were carried out by Mr. W. Cramer on a Mettler Vacuum Thermal Analyzer TA-1. The compounds were heated up to 300 °C at a rate of 8 °C/min in nitrogen atmosphere. Diffuse reflectance spectra were obtained on 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 nujol mulls and Cs I pellets (wavenumber accuracy better than 2 cm^{-1}).

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TABLE I. Analytical Data[a] and Colours.

Compounds	Prep.	M %	C %	H %	N %	Colour
$Cd(NO_2Pz)_2$	1b, 2b	33.5 (33.41)				white
$Zn(NO_2Pz)_2$	1a, 2a	22.6 (22.59)	24.95 (24.86)	1.50 (1.38)	28.90 (29.01)	white
$Cu(NO_2Pz)_2$	1b	22.2 (22.10)				green
$Co(NO_2Pz)_3$	1b	15.3 (14.92)				orange
$Ag(NO_2Pz)$	1a	49.0 (49.06)				white
$Cd(NO_2Pz)_2(NH_3)\cdot H_2O$	1a	30.21 (30.24)	19.34 (19.37)	2.57 (2.42)	26.05 (26.37)	white
$Mn(NO_2Pz)_2(NH_3)\cdot H_2O$	1a	18.0 (17.49)				yellow
$Ni(NO_2Pz)_2(NH_3)_2\cdot 2H_2O$	1a	16.70 (16.65)	20.57 (20.40)	3.85 (3.96)	32.09 (31.74)	grey
$Ni(NO_2Pz)_2\cdot(H_2O)_2$	2b	18.2 (18.42)				green
$Cu(NO_2Pz)_2(NH_3)$	1a	20.38 (20.85)	22.98 (23.62)	2.86 (2.29)	32.50 (32.10)	blue

[a] Calculated values are in parentheses.

Laser-Raman spectra were recorded on a Jeol JRS-4000 Laser-Raman spectrophotometer equipped with a Coherert Radiation CR-2 Argon gas ion laser. 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. Metal analyses were carried out by complexometric titrations after decomposition by heating in nitric acid. Carbon, hydrogen, and nitrogen analyses were carried out by the Microanalytical Department of Organisch Chemisch Instituut TNO, Croesestraat 79 Utrecht, under the supervision of Mr. W. J. Buis.

Results and Discussion

Thermoanalytical Experiments

The compounds $Ni(NO_2Pz)_2(NH_3)_2\cdot 2H_2O$ and $Cu(NO_2Pz)_2(NH_3)$ were subjected to thermoanalytical measurements. The DTG curve of the Ni salt shows a decrease in weight of 9% at 160 °C. This is in agreement with a loss of two mol NH_3 (theor. 9.6%) or H_2O (theor. 10.1%). A strong DTA peak is observed at 156 °C. This peak is probably caused by the transition from $Ni(NO_2Pz)_2(NH_3)_2\cdot 2H_2O$ to the green $Ni(NO_2Pz)_2(H_2O)_2$. In $Ni(BrPz_2(NH_3)_2\cdot 2H_2O$ this transition is found at 200 °C. We therefore assume that the ammonia molecules are lost first and that the removal of the water is taking place in a more moderated way. This is in agreement with the observed infrared and ligand field spectra of the compounds which are dried at 180 °C.

For $Cu(NO_2Pz)_2(NH_3)$ a DTA peak is observed at 250 °C. The DTG curve indicates a loss of weight of 7.5% at 250 °C. We ascribe this transition to the formation of the compound $Cu(NO_2Pz)_2$, with an expected loss of weight of 5.6% for the removal of the NH_3.

Infrared Spectra

The symmetry of NO_2Pz^- with the five-membered ring and NO_2 group in plane is C_s or C_{2v}. Taking the Y-axis perpendicular to the plane and excluding metal–ligand and N–H vibrations in C_{2v} symmetry the normal modes $9A_1$, $8B_1$, $3A_2$ and $4B_2$ are expected.

When the symmetry is C_s, the normal modes are $17A'$ and $7A''$. All fundamentals are active in the Raman spectrum. Only the A_2 modes are infrared inactive.

TABLE II. Infrared and Raman Data (cm^{-1}).[a]

$Zn(NO_2Pz)_2$			Range in Other Salts	HNO_2Pz		DNO_2Pz	$Ni(HNO_2Pz)_4Cl_2$	Description
IR	Raman	Assignment		IR	Raman	IR	IR	
3155 m	–	$A_1 + B_1$	3155–3120	3170 m	–	3170 m	3162 m	C–H stretch
3140 m	–	$\nu_1 + \nu_{10}$	3155–3120	3125 m	–	3140 m	3138 m	C–H stretch
3120 m	–	$2\nu_{11}$			–		3110 m	overtone
				2900 s, br	–		3315/3240 m	N–H stretch
						2200 vs		N–D stretch
1560 m	1550 sh	B_1 ν_{11}	1570–1560	1575 m	1570 m	1560 sh	1560 sh	Ring stretch
1518 vs	1524 s	B_1 ν_{12}	1515–1490	1500 vs	1504 s	1500 vs	1530 vs	N–O stretch asym
	1514 s	A_1 ν_2		1490 sh	1490 sh	1490 sh	1480 s	Ring stretch
1440 m	1435 m	A_1 ν_3	1450–1435	1438 m	1430 sh	1435 m	1430 sh	C–N stretch
1410 s	1410 s	A_1 ν_4	1420–1400	1410 vs	1410 vs	1410 vs	1417 s	Ring stretch
1350 w	1350 m	$\nu_{19} + \nu_{20}$	1360–1330		1355 m		1352 m	overtone
1340 w		$2\nu_{23}$		1302 m			1285 sh	overtone
1290 s	1294 vs	A_1 ν_5	1300–1268	1360 vs	1369 s	1318 s	1339 s	N–O stretch sym + (N–H bending)
1290 s	1294 vs	A_1 ν_6	1290–1250	1290 vs	1286 vs	1290 s	1272 s	C–H bending + Ring
1193 m	1198 m	$A_1 + B_1$	1200–1180	1193 m	1190 s	1190 s	1204 m	Ring + C–H bending
1185 m	1188 m	$\nu_7 + \nu_{13}$	1180–1150	1162 m	1160 m	1220 m	1136 s	Ring + C–H bending + (N–H bending)
1048 s	1050 m	B_1 ν_{14}	1055–1020	1032 s	1035 s	1040 s	1048 s	C–H bending
1008 m	1005 s	A_1 ν_8	1010–1000	998 s	994 s	1000 m	993 s	Ring bending
1000 m		B_1 ν_{15}	1000–970	940 s	947 m	940 m	946 m	Ring bending
						960 m		N–D bending
891/878 m	880 vw	B_2 ν_{18}	895–860	899 s	897 w	911/899 s	911/899 s	C–H bending out of plane
				856 s			740/700 s	N–H bending out of plane
855 vw	855 vw	A_2 ν_{22}	not obs.		840 vw		855 w	C–H bending out of plane
820 s	818 m	A_1 ν_9	820–818	820 s	815 m	820 s	823 s	NO_2 scissoring
755 s	755 w	B_2 ν_{19}	760–750	758 s	756 w	758 s	758 s	NO_2 wagging
						712/677 vs		N–D bending out of plane
670 vw	670 w	A_2 ν_{23}	680–670	652 vw	651 w		641 m	Ring torsion
600 s	600 w	B_2 ν_{20}	605–600	595 s	596 w	593 s	595 s	Ring torsion
555 m	550 m	B_1 ν_{16}	565–555	549 s	546 m	546 s	543 m	NO_2 rocking
475 m	480 w	B_1 ν_{17}	490–400	438 m	439 w	438 m	452 m	C–N bending
296 s	280 s, br	$A_1 + B_1$	540–200				300 m	metal–ligand stretch
267 s	260 s, br						250 m	metal–ligand stretch
240 sh		B_2 ν_{21}	260–230	229 m	235 m	225 m		C–N bending out of plane
–	–	A_2 ν_{24}	–	–	100 s	–	–	NO_2 twisting

[a] s = strong, m = medium, w = weak, sh = shoulder, v = very, br = broad, – = not investigated.

For both the neutral ligand in solid state and the coordinated anion in the solid compounds a C_{2v} symmetry can be concluded from the infrared and Raman spectra (see Table II). For the anion this is in agreement with a bidentate coordination via the nitrogen atoms. In other pyrazoles in the solid state hydrogen bonding causes a 'pseudo C_{2v}' symmetry. The C_{2v} symmetry is distorted by distinction in the N–H bonds. In HNO_2Pz these N–H bonds are probably much more comparable as the low pK_b correlates with weakened N–H bindings and this might explain the C_{2v} symmetry for the neutral ligand in the solid state. In transition metal complexes of the neutral ligand a C_s symmetry is found (Fig. 1a, b, c). In Table II infrared and Raman data of salts of HNO_2Pz are listed, together with data of the complex $NiCl_2$-$(HNO_2Pz)_4$ and the neutral ligand itself.

For the description of the normal vibrations, we used the assignments of pyrazole and halogeno pyrazoles, which we reported in a previous paper [7], as far as the vibrations of the five-membered ring are concerned. For the normal modes associated with the C–NO_2 group assignments of other nitrocompounds as nitromethane [8], nitrobenzene [9–11] and 3-nitrotriazole [12, 13] were compared with the earlier assignment of 4-nitropyrazole reported by Reedijk [3].

The concept for the vibrations of nonsubstituted five-membered rings is based on the following con-

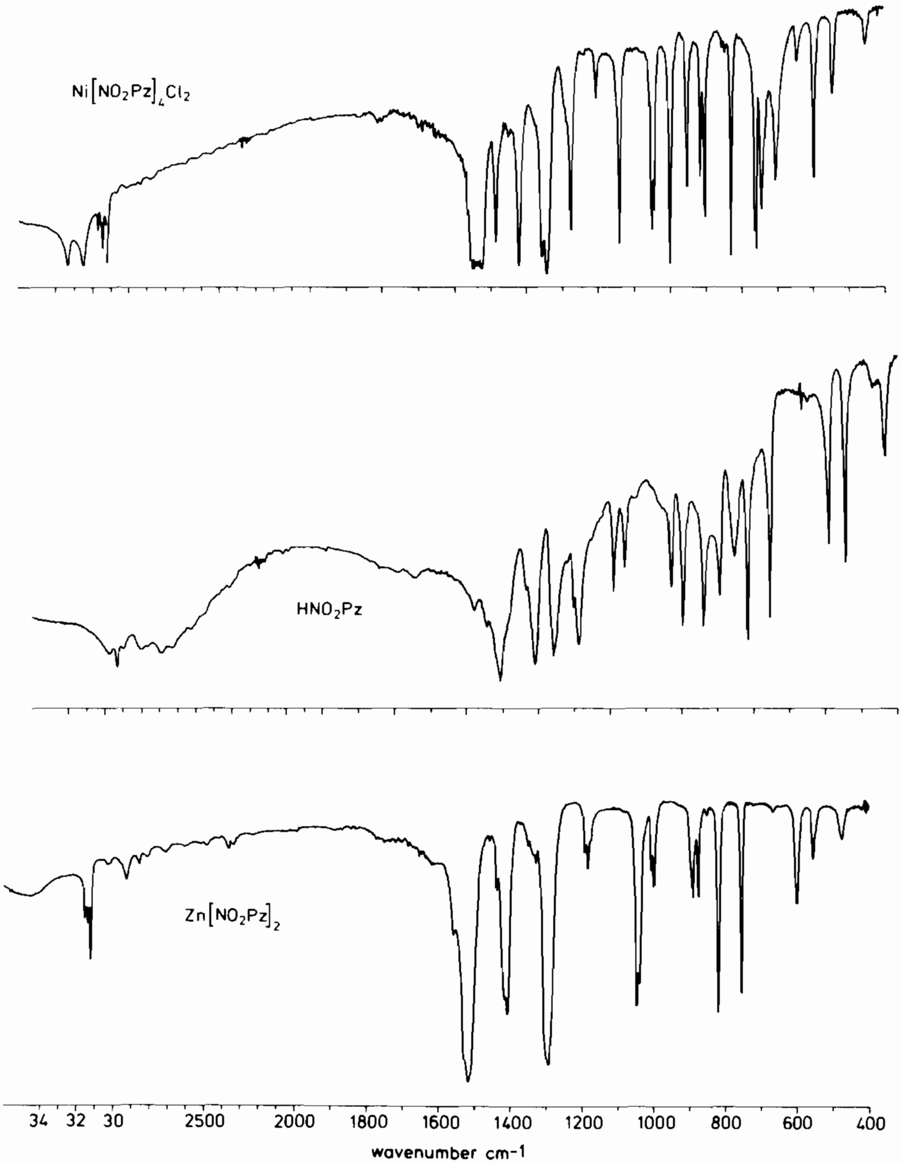

Figure 1. Infrared spectra of $Ni(HNO_2Pz)_4Cl_2$, HNO_2Pz and $Zn(NO_2Pz)_2$ as CsI pellets between 4000–400 cm^{-1}.

siderations. A_1 and B_1 vibrations are usually found at wavenumbers higher than 900 cm^{-1} [3, 6, 14–16]. 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 remaining bands above 900 cm^{-1} are B_1 modes. Differentiation between the A_2 and B_2 modes in the 600–900 cm^{-1} region can easily be made, as the A_2 species are infrared inactive. For a number of vibrations associated with the nitro group the assignments are rather controversial, especially the C–N modes. The νC–N in nitrobenzene for example is found at 850 cm^{-1} according to Stephenson [9] and at 1266 cm^{-1} according to Mooney [10]. In 3-nitrotriazole [12] the νC–N is hold responsible for a band at 1510 cm^{-1}. In this last paper the C–N bond length, based on a X-ray diffraction analysis [13], is reported to be 1.40 Å, in which case the νC–N indeed should be found higher than 1300 cm^{-1} [10]. We therefore attribute a band at 1440 cm^{-1} to the C–N stretch mode. The C–N bending modes are assigned to bands at 480 and 210 cm^{-1} in $Zn(NO_2Pz)_2$, whereas the $-NO_2$ twisting should be found at low wavenumber [11] and is therefore not observed. The other $-NO_2$ vibrations are taken from the literature [8–12].

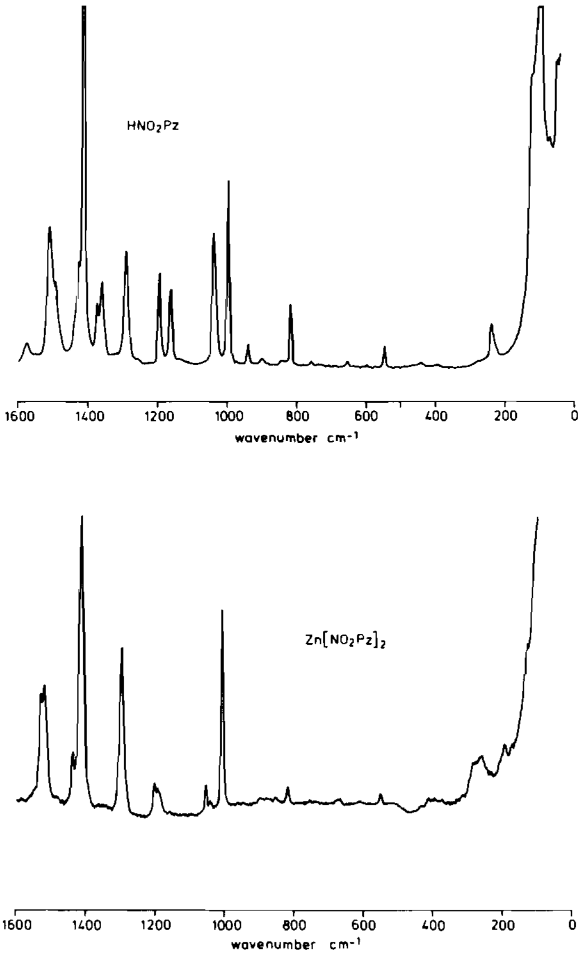

Figure 2. Raman spectra of HNO_2Pz and $Zn(NO_2Pz)_2$ in the solid state between 1600–100 cm^{-1}.

In Table III the NH_3 rocking frequency of a number of compounds is listed. The NH_3 rocking vibration is the most sensitive to the nature of the metal of all NH_3 vibrations: the higher the rocking frequency the stronger the M–NH_3 bond [17].

TABLE III. NH_3 Rocking Frequencies (cm^{-1}).

Compounds	$BrPz^-$ [18]	NO_2Pz^-	$M(NH_3)_6Cl_2$ [17]
Cd(II)	510	560	613
Mn(II)	–	550	617
Co(II)	–	580	654
Ni(II)	560	620	680
Cu(II)	–	670	713[a]

[a] Taken from $Cu(NH_3)_4Cl_2$.

From this data the order of strength of the M–N bond appears to be Cu > Ni > Co > Mn ≈ Cd. In salts of HNO_2Pz the NH_3 molecules are coordinated more strongly than in the salts of halogeno pyrazoles. In all reported compounds the NH_3 rocking vibrations are found at lower wavelengths than in the corresponding hexammine complexes of the metal chlorides [17].

Far-infrared Spectra

Far-infrared spectra were recorded in order to obtain information about the metal–ligand bond. The spectral data are listed in Table IV. As stated in Part I of this series the symmetry round the metal ion is D_{2d}, D_{2h} or D_2, when the ligand is included. In the first two cases, where the nitrogen atoms are coordinating with respectively square-planar and tetrahedral symmetry, two infrared active metal–ligand stretch vibrations are expected. When the direct symmetry round the metal is not D_{4h} or T_d the overall symmetry is D_2 and three metal–ligand stretch bands become infrared active.

The observed metal–ligand bands follow the Irving–Williams sequence, and are found in a region which is normal for nitrogen donor ligands, but at wavelengths higher than in the corresponding complexes of the neutral ligands [3, 18]. The metal–ligand vibrations in nitropyrazole salts occur at lower wavenumbers than in the salts of pyrazole [1]. Differences of about 10 cm^{-1}, which are usually found comparing complexes of the neutral ligands [3], are observed here as well. This shift is probably caused by the lower pK_b of nitropyrazole, but also the higher mass of this ligand might be important. For the Ni salt the observed difference is much larger. This is apparently caused by a different coordination of the metal ion. In $Ni(Pz)_2$, where metal–ligand bands are

TABLE IV. Far-infrared Data (cm^{-1}).

Compounds	Metal–Ligand Vibrations				Ligand Vibrations		
$Cd(NO_2Pz)_2$	230 m	200 m^a			460 m	260 m	
$Cd(NO_2Pz)_2(NH_3)\cdot H_2O$	230 m				460 m	260 m	
$Zn(NO_2Pz)_2$	298 s	266 s			465 m	240 sh	
$Co(NO_2Pz)_2(NH_3)_2\cdot xH_2O^b$	308 s	288 m	260 s			220 w	
$Ni(NO_2Pz)_2(NH_3)_2\cdot 2H_2O$	330 s	308 s	280 s		470 m	250 w	230 w
$Ni(NO_2Pz)_2(H_2O)_2$	330 s	308 s	280 s		480 m	250 w	230 w
$Mn(NO_2Pz)_2(NH_3)\cdot H_2O$	270 s	245 s			470 m		
$Cu(NO_2Pz)_2(NH_3)$	322 m	290 m	278 m	250 s	490 m	230 w	210 w
$Cu(NO_2Pz)_2$	343 s	292 s			498 m		
$Co(NO_2Pz)_3$	534 w	494 m			410 m	250 w	230 w
$Ag(NO_2Pz)$	285 s	250 s			235 sh		

^{a}For the meaning of the symbols used see Table II. ^{b}See experimental part.

TABLE V. Ligand-field Data (kK).

Compounds	Ligand Field Bands			Ir Overtones		
				N–H	C–H	O–H
$Mn(NO_2Pz)_2(NH_3)\cdot H_2O$	–			6.5	6.1	–
$Ni(NO_2Pz)_2(NH_3)_2\cdot 2H_2O$	11.3	17.9		6.5	6.1	–
$Ni(NO_2Pz)_2(H_2O)_2$	10.1	16.3		–	6.1	5.2
$Co(NO_2Pz)_2(NH_3)_2\cdot xH_2O^b$	10.2	19.0 sh	21.0	6.5	6.1	–
$Cu(NO_2Pz)_2(NH_3)$	16.0 asym.			6.5	6.1	–
$Cu(NO_2Pz)_2$	17.4			–	6.2	–
$Co(NO_2Pz)_3$	21.4			–	6.2	–

^{a}For the meaning of the used symbols see Table II. ^{b}See experimental part.

found at 452 and 408 cm^{-1}, a square-planar arrangement is found from the ligand field spectrum.

In $Ni(BrPz)_2(NH_3)_2\cdot 2H_2O$ an infrared band at 320 cm^{-1} has been assigned as a M–NH_3 stretch mode [2]. In the now reported compounds this stretch vibration is expected to occur at about the same wavelength. No definite assignment can be made because other metal–ligand vibrations are present in this region.

Ligand Field Spectra

Ligand field spectra were recorded in order to obtain information about the direct environment of the metal ion. The spectral data are listed in Table V. The ligand field spectrum of the Co(III) salt is in agreement with a low spin octahedral coordinated metal ion. Compared with the Co(III) salts, which we reported earlier, the absorption band which is ascribed to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition shifts to higher wavelengths. So the assumption we made that a lower pK_b induces a higher value for the F_4 parameter seems to be realistic [2]. From the absorption bands of the Co(II) salt (see Experimental) an octahedral coordination of the metal ion is expected.

The calculated spectral parameters [19] are Dq = 1110 cm^{-1} and B = 825 cm^{-1}. From the infrared spectrum and the ligand field spectrum it is evident that the ammonia molecules are coordinated. In the Co(II) salts reported earlier [2], the cobalt ions were coordinated tetrahedrally; no ammonia molecules were present.

The ligand field spectrum of $Ni(NO_2Pz)_2(NH_3)_2\cdot 2H_2O$ indicates octahedral coordinated metal ions. For this mixed complex we calculate [20] Dq = 1130 cm^{-1} and B = 830 cm^{-1}. For $Ni(BrPz)_2(NH_3)_2\cdot 2H_2O$ [2] we observe an almost equal value for Dq (1140 cm^{-1}) and a lower value for B (766 cm^{-1}). With the rule of average environment [21] we calculate a Dq value of 1155 cm^{-1} for the NO_2Pz^- salt; for $BrPz^-$ we found 1170 cm^{-1}.

In $Ni(NO_2Pz)_2(H_2O)_2$ the water is coordinated, which results in a pseudo-octahedral coordination.

The ligand field bands observed for the Cu salts are found at wavelengths which are too high for tetrahedral coordination. From the infrared spectra of the blue Cu(II) salt, coordination of ammonia is evident. We therefore expect a five coordination in this compound. A square-planar coordination is expected for $Cu(NO_2Pz)_2$. NO_2Pz^- seems to coordinate less strongly than the anions we reported before. Instead of a square-planar Ni compound a distorted octahedral coordination is observed and a octahedral Co(II) salt including coordinated NH_3 molecules is found instead of a tetrahedral Co(II) salt. As we stated in the infrared part of this paper, the coordination of ammonia in the salts of HNO_2Pz is stronger than in the salts of the halogenopyrazoles. We might conclude from this that when the anion becomes a weaker ligand the NH_3 molecules are coordinating more strongly and almost identical pseudo octahedral coordinations are obtained. The higher value for B in $Ni(NO_2Pz)_2(NH_3)_2 \cdot 2H_2O$ might be explained by stronger coordinating ammonia molecules as well as by the lower pK_b of the neutral ligand.

Conclusions

(i) In all salts the anion possesses C_{2v} symmetry and therefore acts as a bidentate ligand.

(ii) The low pK_b of HNO_2Pz probably causes weaker coordination of the anion than in salts of pyrazole.

(iii) Because of the weaker coordination of NO_2Pz^- ammonia molecules are taking part in the coordination of the metal ion in a number of salts.

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