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Pyrazolato and Related Anions.
Part I. Bidentate Coordination of the Pyrazolato Ion

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A number of metal salts of pyrazole are reported. Salts of Cd, Zn, Co, Ni and Cu are synthesized from an aqueous ammonia solution, or by addition of NaOH to a solvated pyrazole metal complex in water. The compounds were characterized and identified by chemical analyses, infrared and ligand field spectra. In all cases the pyrazolato ion acts as a bidentate, and tetrahedral or square planar surrounded metal ions are found.

Introduction

Pyrazole (HPz) is a well known monodentate ligand, coordinating *via* the pyridine nitrogen of the ring [1–4]. Because HPz is a weak acid (pK = 14), it is also possible to obtain metal compounds with the pyrazolato ion (Pz). Only a few salts of HPz are known. The preparation of the iron compounds has been published by Seel and Sperber [5]. Monovalent silver and copper salts have been reported by Buchner [6] and Okkersen [7]. Ligand field spectra of Co(II) salts have been reported by Bagley and Nicholls [8]. Magnetic measurements on a compound $Cu(Pz)_2(0.5\ H_2O + 0.5\ NH_3)$ have been performed by Inoue *et al.* [9]. Trofimenko mentioned some unpublished work on Pz compounds [4]. Furthermore, metal salts of imidazole and benzimidazole are known [10–13], systematic investigations on metal–Pz compounds are not available. As a preliminary study to photochemical experiments on HPz salts [14] the preparation and characterization of these compounds is described.

Experimental

Commercially available HPz and metal salts were used without further purification. To obtain the Pz salts two procedures were followed:

1) Addition of the metal salt (hydrated chlorides or nitrates) to HPz, both dissolved in 25% aqueous solution of ammonia.
2) A solution of NaOH was added to a solution of a HPz solvated metal complex (*e.g.* $Cu(HPz)_4Cl_2$) in water.

In both cases the salts were obtained as powders, centrifugated, washed with water, ethyl alcohol and diethyl ether and dried *in vacuo* at 100 °C. The compounds thus obtained are listed in Table I. All compounds are stable up to 250 °C except $Cu(Pz)_2 \cdot H_2O$. The purple $Cu(Pz)_2 \cdot H_2O$ loses ½H_2O at 108 °C and turns brown; no further loss of water has been observed. The compound $Co(Pz)_2$ is sensitive to oxygen in the presence of water, then $Co(Pz)_2OH$ is formed. The yellow Ni salt could be obtained from an ammonia solution (synth. 1) after evaporation of the solvent.

Physical Measurements and Analyses

Diffuse reflectance spectra were obtained in a Beckman DK-2A ratio recording spectrophotometer with MgO as a reference. Infrared spectra were recorded on a Unicam Sp1200 (4000–400 cm^{-1}) and 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 and nitrogen analyses were carried out by the Microanalytical Department of Organisch Chemisch Instituut T.N.O., Croesestraat 79, Utrecht, under supervision of Mr. W. J. Buis.

Results and Discussion

In relation to the synthetic procedures used it is surprising that ligands as NH_3 or H_2O (except for Cu^{2+}) were not included in the obtained compounds. The limitation in the ratio of metal to possible active ligand atoms and limited in degree of freedom of two linked nitrogen atoms situated on one Pz ion are suitable for extra ligand coordination. The reason can only be found in: (a) a well fitting and probably highly symmetric structure; (b) a ligand with a large crystal field splitting, favouring special stable d-electron configurations.

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

Compound	Synth.	Metal %	C %	H %	N %	Colour
$Cd(Pz)_2$	2	44.8 (45.6)				white
$Zn(Pz)_2$	1,2	33.4 (32.8)				white
$Co(Pz)_2$	1,2	30.7 (30.5)	37.04 (37.22)	4.07 (3.13)	28.83 (29.02)	purple
$Ni(Pz)_2$	1,2	30.5 (30.4)	36.99 (37.36)	3.37 (3.14)	27.87 (29.05)	yellow
$Cu(Pz)_2$	2	32.4 (32.2)				black
$Cu(Pz)_2 \cdot H_2O$	1	29.3 (29.5)	33.03 (33.41)	4.15 (3.71)	26.91 (25.99)	purple
$Cu(Pz)_2 \cdot \frac{1}{2}H_2O$		30.8 (30.8)	35.04 (34.87)	3.20 (3.40)	27.37 (27.12)	brown
$Co(Pz)_3$	1	21.8 (22.6)				orange
$Co(Pz)_2OH$		28.0 (28.2)	36.23 (34.46)	3.49 (3.39)	27.27 (26.80)	brown

[a] Calculated values are in parentheses.

The low solubility of the salts prevented the preparation of single crystals. So a structure determination could not be done. The infrared and ligand spectra were investigated to obtain information on the coordination.

Infrared Spectra

The free HPz molecule and HPz as a monodentate ligand [2] in coordination complexes belong to the C_s symmetry point group, for HPz in the solid state, due to H-bond formation [15], the symmetry can be considered approximately C_{2v}. The infrared spectrum of the Pz ion differs from that of HPz not only by the absence of the N–H vibrations but also by a change in symmetry. The symmetry of the free Pz ion is C_{2v} and the out-of-plane A_2 vibrations, taking the X axis perpendicular to the molecular plane, are infrared inactive. In C_s symmetry all vibrations are infrared active.

For Pz^- acting as a bidentate ligand this C_{2v} symmetry may be conserved, as for monodentate Pz^- the symmetry is again C_s.

The out-of-plane vibrations for a number of compounds are listed in Table II. From these data the

TABLE II. Out-of-plane Vibrations.

Assignment [3, 15]	Free HPz	Solid HPz	$Ni(HPz)_6(ClO_4)_2$	$Ni(Pz)_2$	$Zn(Pz)_2$	$Cu(Pz)_2$
	Cs^a	C_{2v}	C_s	C_{2v}	C_{2v}	C_{2v}
C–H bending	879 m	894 s 882 s	868 m	888 m	886 m	870 m
C–H bending	833 m	841 s	795 sh			
C–H bending	744 vs	765 vs	786 s 772 sh	775 s 750 s	778 s 760 s	750 vs
N–H bending	?	?	682 s			
Ring deformation	668 s	665 s	665 sh	(680 w)		
Ring deformation N–H bending	612 s	618 s	575 s, vb	634 s	630 s	630 s 620 s

[a] Proposed symmetry. s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder.

absence of one C–H and one ring vibration in the spectra of the pyrazolato salts is evident. Excluding the free Pz ion according to the ligand field spectra (Table III) a bidentate Pz ligand with C_{2v} symmetry seems realistic.

TABLE III. Ligand Field and Far-infrared Data.

Compound	Ligand Field Bands (kK)		ν(M–N) (cm^{-1})	
$Cd(Pz)_2$			240	v, br
$Zn(Pz)_2$			300	270
$Co(Pz)_2$	8.8	17.5	330	315
$Ni(Pz)_2$	22.2		452	408
$Cu(Pz)_2$	16.0	19.1	365	(285?)
$Cu(Pz)_2 \cdot H_2O$	17.4		355	320
$Cu(Pz)_2 \cdot \frac{1}{2}H_2O$	17.4	20.0	355	320
$Co(Pz)_3$	20.0		495	463

The copper compounds that contain water show some unusual infrared absorptions. We find two sharp bands of medium intensity at 3618 cm^{-1} and 3542 cm^{-1} and a strong sharp band at 1618 cm^{-1}. The spectra of water dissolved in organic solvents in the absence of hydrogen bonding show similar absorptions [16]. Therefore, we suggest that the three absorptions are due to monomeric water molecules.

No clear M–O vibrations could be assigned. $Cu(Pz)_2 \cdot H_2O$ has a very broad band at 350 cm^{-1} and in $Cu(Pz)_2 \cdot \frac{1}{2}H_2O$ only a broadening of the M–N bands has been found. From ligand field spectra, however, it is obvious that the water is coordinated to the metal.

Far-infrared Spectra

Far-infrared spectra were recorded in order to obtain information on the metal–ligand bond. M–N stretching vibrations are listed in Table III. These bands are found in the usual range for nitrogen donor ligands at higher wave numbers than in the HPz complexes [1–4]. The metal–ligand bands follow the Irving–Williams series. A higher value for the Ni compound than for the other species suggests a square planar coordination.

In the model including the metal ion and the donor atoms the symmetry is T_d or D_{4h} (according to the ligand field spectra), only one ML stretching is expected to occur. The symmetry around the metal including the ligand is D_{2d} or D_{2h}. In both point groups two ML stretching vibrations are infrared active. When the coordination around the metal ion is not exactly T_d or D_{4h} the symmetry including the ligand is D_2 and three ML stretching bands are expected. In all compounds we find split bands, therefore the distortions from T_d or D_{4h} coordination in the metal–nitrogen skeleton are probably small.

Ligand Field Spectra

The ligand field absorption bands are listed in Table III. The Co(II) compound is coordinated tetrahedrally with Dq = 500 cm^{-1} and B = 750 cm^{-1}. These values are in reasonable agreement with those obtained by Bagley [8] and stand for a ligand ranking high in the spectrochemical series (higher than NH_3 and HPz). For this reason Co(II) in those systems is so easily oxidized by oxygen to Co(III). The ligand field spectrum of $Co(Pz)_3$ is in agreement with a low-spin octahedral coordinated Co(III) ion.

Information on the coordination in the Zn and Cd compounds can be obtained by using Co(II) dopes. A dope of Co(II) in $Zn(Pz)_2$ showed tetrahedrally surrounded Co(II) ions almost identical with the results obtained from pure $Co(Pz)_2$. We suggest that $Zn(Pz)_2$ is a tetrahedral complex.

No dope of Co(II) in $Cd(Pz)_2$ could be obtained; the result was an oxidation of the cobalt to Co(III) as mentioned before. The M–N spectrum for $Cd(Pz)_2$ (Table III) deviates from the other compounds as well.

These observations are in agreement with the fact that the two compounds are not isomorphous [14] and we do not expect a tetrahedral coordination for $Cd(Pz)_2$.

The absorption band of the Ni(II) compound is assigned to the ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition in a square planar arrangement [17]. $Ni(Pz)_2$ is diamagnetic [14], supporting this arrangement.

The absorptions of the copper compounds cannot be assigned to tetrahedral Cu(II) species. We surmise a square planar coordination for Cu(II) in $Cu(Pz)_2$. When in the hydrated compounds the Pz ions are coordinated in the XY plane, then the water can be bound in the Z direction. In $Cu(Pz)_2 \cdot H_2O$ a symmetric absorption at 17.4 kK is observed, assigned to a distorted octahedron with water bridging between two copper ions. $Cu(Pz)_2 \cdot \frac{1}{2}H_2O$ shows a band at 20.0 kK and a shoulder at 17.4 kK. In the latter compound the Cu(II) ion may be 5-coordinated.

The infrared spectra show that the Pz ion acts as a bidentate. Therefore, the metal ion is coordinated by four nitrogen atoms. Probably the Pz ion is bridging two metal atoms resulting in a chain structure. This is in agreement with EPR spectra of the copper salts which show strong metal–metal interactions. Considering the possibility of a rotation of the ligands around the metal–metal axis, we get a range of structures with the tetrahedral and square planar arrangements as extremes.

Conclusions

As a result of our investigations we can draw the following conclusions: (i) In all our compounds the

Pz ion acts as a bidentate. (ii) A chain structure with tetrahedral or square planar surrounded metal ions is the most probable.

Note

A complete assignment of the infrared spectra and magnetic measurements of the compounds described above will be published shortly. Further investigations will be performed on the salts of derivatives of pyrazole including halo-pyrazoles, alkyl-pyrazoles and nitro-pyrazoles. We are also studying salts of triazoles and their derivatives.

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