^{1}H NMR Studies of Some Pyrazole Ligands Coordinated to Co(III)

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Summary: Proton chemical shifts of pyrazole ligands coordinated to Co(III) move downfield as the total charge of complex increases. However ^{1}H chemical shifts of pyrazole ring in $[Co(NH_3)_5(pyzH)]^{3+}$ and $[Co(NH_3)_5(pyz)]^{2+}$ compare to those of $pyzH_2^+$ with one positive charge move upfield. These unexpected phenomena together with facile nitration and bromination of $[Co(NH_3)_5(pyzH)]^{3+}$ compare to nitration and bromination of free pyrazole or its protonated form under forcing conditions could be related to more electron releasing of $Co(NH_3)_5^{3+}$ group relative to H^+.

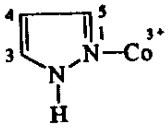
Introduction

Coordination of a ligand to a metal ion, such as Co(III), can make appreciable changes in ^{1}H chemical shift and reactivity of the ligand, which may be important to understanding of certain biological processes. Nuclear magnetic resonance (NMR) is just a technique, which has been used widely to study of these changes [1-10]. ^{1}H NMR studies of some heteroaromatic ligands coordinated to different metal ions has been shown that many factors including magnetic anisotropy, temperature paramagnetism, σ-effect and π-back bonding may influence the NMR chemical shifts of proton in nitrogen heterocycles coordinated to metal ion. Among these the σ-effect and π-back bonding are the most important factors which are sufficient to explain all differences between ^{1}H chemical shifts of free ligands and their coordination forms [11].

We are going to report ^{1}H chemical shift changes of pyrazole ligands coordinated to Co(III) as well as facile nitration and bromination of $[Co(NH_3)_5(pyzH)]^{3+}$ with consideration of potential influences due to this coordination.

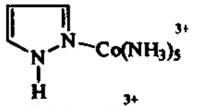
Results and Discussion

Numbering system for pyrazole ring coordinated to Co(III) is shown as:

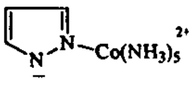


while the free ligand is numbered such that the protonated nitrogen is designated as N-1.

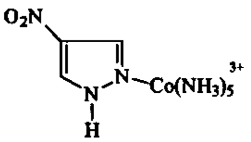
Table-1 summarizes ^{1}H NMR chemical shifts of pyrazole ligands coordinated to Co(III) (1-4), free pyrazole and its protonated form in D_2O.


$[Co(NH_3)_5(pyzH)]^{3+}$

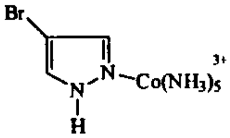
1


$[Co(NH_3)_5(pyz)]^{2+}$

2


$[Co(NH_3)_5(4\text{-}NO_2\text{-}pyzH)^{3+}$

3


$[Co(NH_3)_5(4\text{-}Br\text{-}pyzH)]^{3+}$

4

Table-1 ^{1}H NMR shift (δ) of Co(III) pyrazole complexes, free pyrazole and its protonated form.

Compound	$C_{(5)\text{-}H}$	$C_{(3)\text{-}H}$	$C_{(4)\text{-}H}$
pyzH	7.70	7.70	6.45
$PyzH_2^+$	8.15	8.15	6.80
$[Co(NH_3)_5(pyzH)]^{3+}$	7.95	7.75	6.68
$[Co(NH_3)_5(pyz)]^{2+}$	7.80	7.59	6.50
$[Co(NH_3)_5(4\text{-}NO_2\text{-}pyzH)]$	8.80	8.70	-
$Co(NH_3)_5(4\text{-}Br\text{-}pyzH)]$	8.45	8.15	-

Coordination between metal ion and ligand causes changes in the chemical shift of ^{1}H NMR of ligands. Several, groups have discussed many factors,

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which may influence the NMR chemical shifts of protons in nitrogen heterocyclic ligands coordinated to the metal ion [1-9,12,13]. σ-Effect decreases the electron density from the ligand, which makes a downfield shift. Opposing this π-back-bonding from the metal *d* orbitals into the ligand π system increases π density of the ring carbons which in turn causes an upfield change in chemical shift of the ring protons. At the remote positions the σ effect is small and shielding is expected for metals that have significant π-back bonding to the ligand [14].

Definite trend in the direction of these effects is clear. Coordination of pyrazole to the metal centre disturbs its symmetry and thus the ^{1}H NMR spectrum of $[Co(NH_3)_5(pyzH)]^{3+}$ display three signals corresponding to three different protons. As table-1 shows, except for $[Co(NH_3)_5(pyz)]^{2+}$, all of the proton resonances of pyrazoles coordinated to Co(III) appear downfield from those of free ligands as a result of σ-donation. In $[Co(NH_3)_5(pyz)]^{2+}$ the anion present on the pyrazole ring increases the electron density which causes an upfield shift. Also the results show that the chemical shifts for $C_{(5)\text{-}H}$ and $C_{(3)\text{-}H}$ in $[Co(NH_3)_5(4\text{-}NO_2\text{-}pyzH)]^{3+}$ and $[Co(NH_3)_5(4\text{-}Br\text{-}pyzH)]^{3+}$ move downfield compare to those of $[Co(NH_3)_5(pyzH)]^{3+}$ due to direct correlation between the electronegativity of the substituent and the chemical shifts of ring protons.

Another interesting point is that the chemical shift of $C_{(2)\text{-}H}$ in $[Co(NH_3)_5(pyzH)]^{3+}$ and $[Co(NH_3)_5(pyz)]^{2+}$ despite of the three and two positive charges relative to chemical shift of $C_{(2)\text{-}H}$ in $pyzH_2^+$ moved upfield. This trend may serve that $Co(NH_3)_5]^{3+}$ group is more electron donating relative to H^+ [15].

Presence of a pyridine-like nitrogen in pyrazole decreases its reactivity towards electrophilic reaction such as nitration and bromination. However coordination of pyrazole to $Co(NH_3)_5]^{3+}$ group makes it very reactive for nitration and bromination. Due to protonation of pyrazole its niration take places under forcing conditions and produce 4-nitro-pyrazole which is in contrast to the facile nitration of $Co(NH_3)_5(pyzH)]^{3+}$ nitration at 0°C to produce $[Co(NH3)_5(4\text{-}NO_2\text{-}pyzH)]^{3+}$. This facile bromination of $[Co(NH_3)_5(pyzH)]^{3+}$ could also be attributed to more electron-rich nature of $Co(NH_3)_5^{3+}$ group.

Experimental

General Experimental

NMR spectroscopies (^{1}H and ^{13}C) together with microanalytical results were used to identification of all compounds. All spectra were recorded in D_2O using either a Bruker 200 or 100 (MHz). ^{1}H chemical shifts (ppm) are referenced to the internal standard 3-(trimethylsilyl)-2,2,3,3-tetra deuteropropionic acid, sodium salt (TSP). Dioxane (67.4 ppm) was also used as a reference for all carbon spectra.

Synthesis of $[Co(NH_3)_5(pyzH)](ClO_4)_3$

A solution of $[(NH_3)_5Co(DMSO)]^{3+}$ (5 g), prepared by method of Buckingham *et al.*, [16], and pyrazole (2.5 g) in dry dimethyl sulfoxide (25 ml) was stirred at 70-80 °C for 45 min and then diluted with water to 1L. The orange solution was subjected to a column of Dowex 50W x 2 cation exchange resin (H^+ form) which then washed with water, and impurities were removed by elution with 1-2 M HCl. The orange-yellow band was eluted with 4M HCl. The orange solution was taken to dryness under reduced pressure, and the solid crystallized from hot water by adding $NaClO_4$ solid. The orange product was washed with ethanol and dried in air (yield 60%). Anal.Calcd for $C_3H_{19}N_7CoCl_3O_{12}$: C, 7.06; H, 3.76; N, 19.21; Cl, 20.83%. Found: C, 7.20; H, 3.84; N, 19.11; Cl, 20.90%. ^{1}H NMR (D_2O): δ = 7.95 (doublet, 1H), 7.70 (doublet, 1H), 6.65 (multiplet, 1H). ^{13}C NMR (D_2O): δ = 144.86, 137.81, 110.51.

Synthesis of $[Co(NH_3)_5(pyz)]\ (ClO_4)_2$

This complex was prepared by reaction of $[Co(NH_3)_5(pyzH)]^{3+}$ and equimolar sodium hydroxide 0.1 M. On addition of sodium perchlorate precipitated the titled compound which was washed with ethanol and air dried (yield 80%). Anal.Calcd for $C_3H_{18}N_7CoCl_2O_8$: C, 8.79; H, 4.43; N, 23.91; Cl, 17.29%. Found: C, 8.27; H, 4.48; N, 23.37; Cl, 17.40%. ^{1}H NMR (D_2O, pD > 10): δ = 7.80 (doublet, 1H), 7.59 (doublet, 1H), 6.50 (multiplet, 1H).

2.4. Synthesis of $[Co(NH_3)_5(4\text{-}NO_2\text{-}pyzH)](NO_3)_3$

To a nitrating mixture including concentrated H_2SO_4 (3.5 ml) and concentrated HNO_3 (0.6 ml), which kept in ice bath (10-15 °C), 0.3 g of $[Co(NH_3)_5(pyzH)]Cl_3$ was added with stirring. After 30 min the reaction mixture was diluted with ice-cooled water to 100 ml. The solution was subjected to a column of Dowex 50W x 2 cation exchange resin (H^+ form), which was then washed with water, impurities were removed by elution with 1 M HNO_3. The orange band was eluted with 4 M HNO_3. The orange solution was taken to dryness under reduced pressure, and washed with ethanol and dried in air (yield %76). Anal.Calcd for $C_3H_{18}N_{11}CoO_{11}$: C, 8.13; H, 4.06; N, 34.76%. Found: C, 8.25; H, 4.40; N, 34.51%. ^{1}H NMR (D_2O): δ = 8.8 (singlet, 1H), 8.7 (singlet, 1H). Due to low solubility of the compound in D_2O it was not possible to obtain a satisfactory ^{13}C NMR spectrum.

Synthesis of [Co(NH$_3$)$_5$(4-Br-pyzH)](ClO$_4$)$_3$

To a well-stirred solution of $[Co(NH_3)_5(pyzH)]Cl_3$ (0.5 g) in HCl 2M (30 ml) was added aqueous Br_2 (excess equimolar) more than 5 min. Stirring continued for 20 min and then was added concentrated HBr (50 ml). The mixture was cooled in ice, and the solid collected by filtering. The product was dissolved in 200 ml water and subjected to Dowex 50W x 2 cation exchange resin (H^+ form) which then washed with water and 1-2 M HCl. The titled complex was eluted with 4 M HCl and the orange solution taken to dryness under reduced pressure. The complex was recrystallized from hot water by adding $NaClO_4$ and cooling (yield 60%). Anal.Calcd for $C_3H_{18}N_7CoO_{12}Cl_3Br$: C, 6.11; H, 3.05; N, 16.62; Cl, 18.07; Br, 13.57%. Found: C, 6.36; H, 3.42; N, 16.49; Cl, 18.15; Br, 13.50%. ^{1}H NMR (D_2O): δ = 8.45 (broad singlet, 1H), 8.15 (broad singlet, 1H). ^{13}C NMR (D_2O): δ = 145.8, 142.85, 138.93.

Conclusions

With the present experimental data, $[Co(NH_3)_5(pyzH)](ClO_4)_3$, $[Co(NH_3)_5(pyzH)](ClO_4)_2$, $[Co(NH_3)_5(4\text{-}NO_2\text{-}pyzH)](NO_3)_3$ and $[Co(NH_3)_5(4\text{-}Br\text{-}pyzH)](ClO_4)_3$ were synthesized.

In all Co(III) coordinated pyrazoles, except for $[Co(NH_3)_5(Im)]^{2+}$, the chemical shifts for protons in all positions are shifted downfield compare with their free ligands, as a result of σ-donation.

The $[Co(NH_3)_5(pyzH)](ClO_4)_3$ undergoes nitration and bromination under very easy condition compare to free pyrazole or its protonated form due to having electron donating group $Co(NH_3)_5^{3+}$.

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