

Behaviour of Some Pyridine Ligands Coordinated to Co(III) in Alkaline Solution

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[Co(NH₃)₅L](ClO₄)₃ (L = pyridine, 2-, 3-, and 4-methylpyridine) were synthesized by reaction of [(NH₃)₅Co(DMSO)(ClO₄)₃] and an appropriate ligand in DMSO solution at 80–85°C. The behaviour of these complexes in alkaline solution indicated that there is no evidence for the possibility of covalent hydration or pseudobase formation. However, under alkaline solution (D₂O/OD⁻) deuterium exchange is the only possibility which can occur on the ortho positions of pyridine ligands coordinated to Co(III).

Key Words: Complex, Heterocycle, Ligand, Pseudobase, Pyridine.

INTRODUCTION

It is well known that addition of hydroxide ion to electron-deficient quaternized aza-heterocycles such as N-methoxy pyridinium^{1,2} and N-alkylquinolinium³ cation results in formation of neutral pseudobase compounds. This process is well documented and several reviews are available⁴⁻⁶. Over the past few years Gillard and coworkers⁷⁻¹⁰ have proposed that coordination of a heterocycle to a transition metal has an effect similar to quaternization, and that such coordinated heterocycles are activated towards pseudobase formation. However, this proposal has been the subject of prolonged controversy for which numerous groups have suggested alternative explanation for the anomalous behaviour of a number of transition-metal heterocycle complexes. Several authors have reviewed this theory^{6, 11-13}. The first paper outlining evidence for covalent hydration of metal-coordinated heterocycles published by Gillard and Lyons⁷ in 1973, although a suggestion of such behaviour was made in 1969 by Gillard and Heaton¹⁴.

In the present paper we report the behaviour of some pyridine ligands coordinated to Co(III) in alkaline solution in order to prove or disprove pseudobase formation in these systems.

EXPERIMENTAL

NMR spectroscopies (^1H and ^{13}C) were used to identify all the compounds. All the spectra were recorded in DMSO using either a Bruker 200 or 100 (MHz) NMR instrument. ^1H and ^{13}C chemical shifts (ppm) are referenced to the internal standard tetramethylsilane (TMS).

[Co(NH₃)₅(py)](ClO₄)₃

A solution of [(NH₃)₅Co(DMSO)](ClO₄)₃ (1.92 g), prepared by method of Buckingham *et al.*¹⁵, and pyridine (0.39 g) in dry dimethyl sulfoxide (5 mL) was stirred at 80–85°C for 1 h and then diluted with water to 1 L. The orange solution was loaded to a column of Dowex 50W × 2 cation exchange resin (H⁺ form) which was then washed with water, and impurities were removed by elution with 1–2 M HCl. The orange-yellow band was eluted with 3–5 M HCl. The orange solution was taken to dryness under reduced pressure, and the solid crystallized from hot water by adding NaClO₄ solid. The orange product was washed with ethanol and dried in air (yield 62%). The IR and NMR studies gave the following results: IR (KBr) = 3277.3, 3146.2, 1635.6, 859.9 cm⁻¹. ^1H NMR (DMSO): δ = 8.56 (m, 2H), 7.88 (m, 1H), 7.46 (m, 2H). ^{13}C NMR (D₂O): δ = 153.4, 142.6, 129.2.

[Co(NH₃)₅(2-Mepy)](ClO₄)₃

A mixture of [(NH₃)₅Co(DMSO)](ClO₄)₃ (1.92 g) and 2-methylpyridine (0.29 g) in dry dimethyl sulfoxide (5 mL) was stirred at 80–85°C for 8 h and then diluted with water to 1 L. Thereafter, exactly same experimental procedures, as reported in synthesis of [Co(NH₃)₅(Py)](ClO₄)₃, were followed. The yellow product was washed with ethanol and dried in air (yield 62%). The IR and NMR studies gave the following results: IR (KBr) = 3350.6, 3219.4, 1635.7, 817 cm⁻¹. ^1H NMR (DMSO): δ = 8.59 (m, 1H), 8.10 (d, 1H), 7.62 (m, 1H), 7.17 (t, 1H), 2.42 (s, 3H). ^{13}C NMR (DMSO): δ = 168, 165.9, 152.1, 134.1, 131.2, 31.6.

[Co(NH₃)₅(3-methylpy)](ClO₄)₃

A solution of [(NH₃)₅Co(DMSO)](ClO₄)₃ (1.92 g), 3-methylpyridine (0.29 g) in dry dimethyl sulfoxide (5 mL) was stirred at 80–85°C for 3 h and then diluted with water to 1 L. Thereafter, exactly same experimental procedures, as reported in synthesis of [Co(NH₃)₅(Py)](ClO₄)₃, were followed. The orange product was washed with ethanol and dried in air (yield 71%). The IR and NMR studies gave the following results: IR (KBr) = 3293.6, 3186.6, 1637.7, 835 cm⁻¹. ^1H NMR (DMSO): δ = 8.70 (br, 2 H), 8.30 (m, 1H), 7.86 (m, 1 H), 2.45 (s, 3 H). ^{13}C NMR (DMSO): δ = 154.7, 151.7, 141.0, 137.0, 126.7, 18.9.

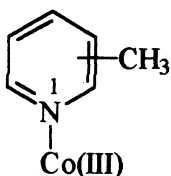
[Co(NH₃)₅(4-methylpy)](ClO₄)₃

A solution of [(NH₃)₅Co(DMSO)](ClO₄)₃ (1.92 g), 3-methylpyridine (0.29 g) in dry dimethyl sulfoxide (5 mL) was stirred at 80–85°C for 3 h and then diluted with water to 1 L. Thereafter, exactly same experimental procedures, as reported in synthesis of [Co(NH₃)₅(py)](ClO₄)₃, were followed. The orange product was washed with ethanol and dried in air (yield 75%). The IR and NMR studies gave the following results: IR (KBr) = 3456.8, 3230.9, 1628.9, 826.9 cm⁻¹. ^1H NMR

(DMSO): $\delta = 8.23$ (m, 2H), 7.60 (m, 2H), 3.44 (s, 3H). ^{13}C NMR (DMSO): $\delta = 154.0, 152.5, 128.5, 12.0$.

RESULTS AND DISCUSSION

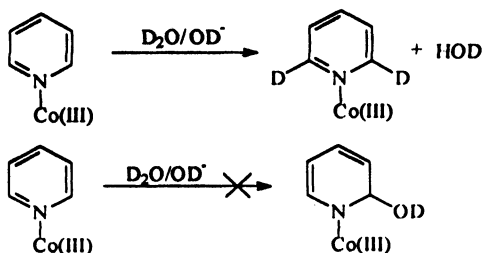
Numbering system for pyridine ring coordinated to Co(III) is shown as:



in which the nitrogen atom coordinated to the Co(III) is called N-1.

^1H and ^{13}C NMR chemical shifts of complexes and uncoordinated ligands are quite different. The IR spectra of complexes exhibited absorption at $3457\text{--}3293\text{ cm}^{-1}$ which is the characteristic of —NH_3 groups. Also absorption at $1638\text{--}1628\text{ cm}^{-1}$ is assigned to $\text{C}=\text{C}$ of the aromatic ring. The IR absorption band in the range of $860\text{--}817\text{ cm}^{-1}$ is assigned to out-plane bending of =C—H of the pyridine ring.

No evidence for pseudobase formation in pyridine ligands coordinated to Co(III) even in strong alkaline solution was observed. H/D exchange at the ortho positions of the quaternized nitrogen was the only process that was observed in these complexes (Scheme-1). Also H/D exchange in these complexes was quite slow than that in N-methylpyridinium perchlorate ($k_{\text{ex}} = 4 \times 10^{-4}\text{ M}^{-1}\text{ s}^{-1}$).



Scheme-1

When a pseudobase is formed from unsaturated heterocyclic cation there are significant changes to the ^1H NMR spectrum. Saturation of a ring carbon atom as a result of pseudobase formation results in an upfield shift up to 4 ppm for a signal of the hydrogen atom attached to that carbon atom⁴. Such a change has not been observed in ^1H NMR spectrum of alkaline solution of all the synthesized pyridine complexes.

It is well known that coordination of a ligand to a metal ion, such as Co(III), can make appreciable changes in the electron density and reactivity of the ligand. σ -Effect decreases the electron density from the ligand. Opposing this π -back-bonding from the metal d orbitals into the ligand π system increases π density of the ring carbons¹⁶. Thus, a predominance of one of these factors will result in

activation or deactivation of pseudobase formation. The ^1H and ^{13}C NMR chemical shifts indicate that coordination of pyridine ligand to $\text{Co}(\text{NH}_3)_5^{3+}$ moiety does activate the ligand towards nucleophilic attack, but it is not clear how great this activation is. The pyridine ligands coordinated to $\text{Co}(\text{III})$ do not undergo electrophilic reactions such as bromination and nitration even under force conditions. This means that π -back-bonding from the metal d orbitals into the ligand π system is not significant and the σ -effect is more important in these complexes. However, reduction of electron density by σ -effect is not as strong to lead pseudobase formation and H/D exchange is the only process which can occur at low rate in strong alkaline solution.

Also it is well known that N-methylpyridinium cation does not produce a pseudobase in strong alkaline solution¹³, but N-methoxypyridinium ion forms a pseudobase^{1,2} as a result of more polarizing ability of $-\text{OCH}_3$ group compared to $-\text{CH}_3$ group. It has been suggested that polarization of charge bond depends on the charge volume ratio, and the polarization of $\text{Co}(\text{NH}_3)_5^{3+}$ group is less than $-\text{CH}_3^+$ group¹⁷. Since N-methylpyridinium cation does not make a pseudobase in strong alkaline solution, clearly it is not expected that $\text{Co}(\text{NH}_3)_5\text{L}(\text{ClO}_4)_3$ (L = a pyridine ligand) makes a pseudobase in alkaline solution.

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