

^1H NMR Studies of Some Imidazole Ligands Coordinated to Co(III)

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Received 27.02.2002

Chemical shifts for proton signals of an imidazole ring coordinated to Co(III) move downfield as the total complex charge increases. However, the $C_{(2)-H}$ chemical shift of the imidazole ring in $\text{cis}[\text{Co}(\text{en})_2(\text{N-mIm}) \text{OPO}_3\text{H}]^\ominus$, which has no charge compared to those of $\text{cis}[\text{Co}(\text{en})_2(\text{N-mIm}) \text{OPO}_3\text{H}]^+$ and $\text{cis}[\text{Co}(\text{en})_2(\text{N-mIm}) \text{OPO}_3\text{H}_2]^{2+}$, moves downfield. These unexpected phenomena could be attributed to an intramolecular interaction between the phosphate anion group and $C_{(2)-H}$ of the imidazole ligand.

Introduction

Coordination of a ligand to a metal ion can cause significant changes in the ^1H chemical shift and reactivity of the ligand. Nuclear magnetic resonance (NMR) spectroscopy has been used widely to study these changes¹⁻⁸. Henderson et al.⁸ have studied the ^1H NMR of some heteroaromatic ligands parallel to the study of the coordination of these ligands to a metal ion. They suggested that the σ -effect and π -back bonding are the most common factors and are sufficient to explain all differences between the ^1H chemical shifts of free ligands and their coordinated forms. The present work discusses the ^1H chemical shift changes of some imidazole ligands coordinated to Co(III) with consideration of potential influences due to this coordination. Some of these influences are the intramolecular interaction between two ligands, and the total charge of the complex. The chemical shift changes are even more dependent on the efficiency of the intramolecular interaction than the total charge of the complex.

Experimental

$[(\text{NH}_3)_5\text{Co}(\text{HIm})]^{3+}$ and $[(\text{NH}_3)_5\text{Co}(\text{mIm})]^{3+}$ complexes were prepared by the reaction of $[(\text{NH}_3)_5\text{Co}(\text{DMSO})]^{3+}$ in dimethyl sulfoxide (DMSO) with imidazole and 1-methylimidazole respectively⁹.

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$[(\text{NH}_3)_5\text{Co}(\text{Im})]^{2+}$ was prepared by the reaction of $[(\text{NH}_3)_5\text{Co}(\text{HIm})]^{3+}$ and sodium hydroxide (equimolar). On the addition of sodium perchlorate the title compound precipitated⁹. The reaction of $[(\text{NH}_3)_5\text{Co}(\text{Im})]^{2+}$ with $[(\text{NH}_3)_5\text{Co}(\text{DMSO})]^{3+}$ in DMSO led to the preparation of $[(\text{NH}_3)_5\text{CoImCo}(\text{NH}_3)_5]^{5+}$.

Cis- $[(\text{en})_2\text{Co}(\text{N-MeIm})\text{OPO}_3\text{H}_2]\text{Br}_2$

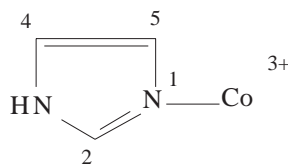
$[(\text{en})_2\text{Co}(\text{N-MeIm})\text{Br}]\text{Br}_2$ (2.50 g) and anhydrous AgClO_4 (3.2 g) were dissolved in 20 mL of 85% H_3PO_4 and stirred at room temperature for 60 h. A small amount of NaCl solution was then added to precipitate the remaining Ag^+ . The mixture was filtered and the filtrate loaded onto PyH^+ form Dowex 50W x 2 IE resin. The column was washed with water and then eluted with pyridinium acetate to remove the major red band. This fraction was taken to dryness at 40°C under reduced pressure. The residue was taken up in water, and LiClO_4 and ethanol were added. The precipitated complex was recovered by filtration. The complex was converted to the Br^- salt by passage down Br^- form Amberlite IRA 400 IE resin. The eluate volume was reduced and then HBr was added to pH ~1. To this solution (10-15 mL) was added ethanol (60 mL) with stirring. The mixture was chilled in ice, and the product recovered by filtration. It was washed with ethanol and then with acetone, and air dried (1.80 g, 69%). $\text{C}_8\text{H}_{24}\text{N}_6\text{O}_4\text{PCoBr}_2$: C, 18.55; H, 4.67; N, 16.22; P, 5.98; Br, 30.85%. Found: C, 18.62; H, 4.58; N, 15.56; P, 5.91; Br, 30.97%. ¹H NMR(D_2O): $\delta = 8.07$ (s, 1H), 7.37 (s, 1H), 7.18 (s, 1H), 3.86(s, 3H), 2.97-2.10 (m, 8H). ¹³C NMR (D_2O): $\delta = 142.1, 128.8, 125.4, 46.18, 45.68, 45.47, 44.7, 36.1$. This complex has three different charges (0, 1, 2), depending on pH.

Physical measurements

NMR spectra (¹H and ¹³C) and microanalytical results were used to identify the complexes (**1-5**). Proton signals of the imidazole ring in these complexes were identified by nuclear Overhauser enhancement (NOE) and heteronuclear correlation (HETCOR) spectroscopies. All spectra were recorded in D_2O on a Varian VXR 300 or Gemini 200(MHZ). 3-(Trimethylsilyl)-2,2,3,3-tetra deuteriopropionic acid, sodium salt (TSP) was used as an internal standard and the chemical shifts are reported on the δ scale.

Results and Discussion

The numbering system for the imidazole ring coordinated to Co(III) is shown as:

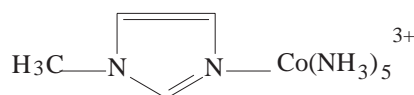


while the free ligand is numbered such that the protonated or alkylated nitrogen is designated as N-1.

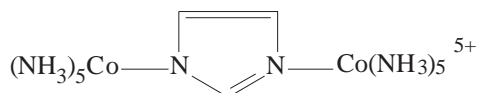
The Table shows ¹H NMR chemical shifts of free imidazole ligands and their coordinated forms to Co(III) (**1-5**).



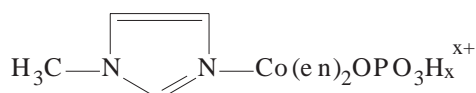
(1)



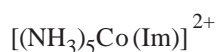
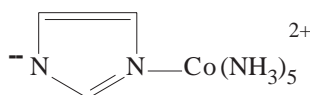
(2)



(3)



(4) $x = 0, 1, 2$



(5)

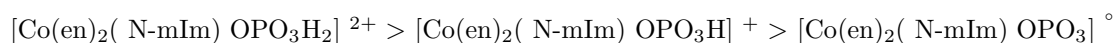
Table. ¹H NMR shift of Co(III) imidazole complexes and their related free ligands.

Compound	C _{(2)-H}	C _{(4)-H}	C _{(5)-H}
$[(\text{NH}_3)_5 \text{Co}(\text{mIm})]^{3+}$	7.99	7.41	7.06
$[(\text{NH}_3)_5 \text{Co}(\text{HIm})]^{3+}$	8.06	7.47	7.09
$[(\text{NH}_3)_5 \text{Co}(\text{Im})]^{2+}$	7.44	7.24	6.92
ImH	7.70	7.03	7.03
ImH ₂ ⁺	8.60	7.40	7.40
N-CH ₃ Im	7.59	7.00	7.08
$[(\text{NH}_3)_5 \text{CoImCo}(\text{NH}_3)_5]^{5+}$	7.86	7.16	7.16
Cis-[Co(en) ₂ (N-mIm) OPO ₃ H ₂] ²⁺	8.07	7.37	7.18
Cis-[Co(en) ₂ (N-mIm) OPO ₃ H] ⁺	8.26	7.33	7.21
Cis-[Co(en) ₂ (N-mIm) OPO ₃] ⁰	8.27	7.33	7.21

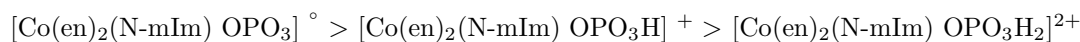
Complexation between metal and ligand causes changes in the chemical shift of ¹H NMR of ligands. A number of factors which may influence the NMR chemical shifts of protons in nitrogen heterocycles coordinated to the metal ion have been discussed by several groups^{1-8,10,11}. A decrease in the electron density of the imidazole ring by the σ effect yields downfield shifts at all ring positions, which is inversely proportional to distance. Opposing this π -back-bonding from the metal d orbitals into the ligand π system increases the π density of the ring carbons, which in turn causes an upfield change in the 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 ligand¹².

In all Co(III) coordinated imidazole and methylimidazole except for [Co(NH₃)₅(Im)]²⁺ the chemical shifts for protons in all positions are shifted downfield compared with their free ligands, as a result of σ -donation. In [Co(NH₃)₅(Im)]²⁺ the negative charge present on the imidazole ring increases the electron density, which in turn causes an upfield shift. The results also show that the chemical shifts for C_{(2)-H} and C_{(H)-5} in [Co(NH₃)₅L]ⁿ⁺ (L = Imidazole) move downfield as the total complex charge increases. As all NH₃ ligands in [Co(NH₃)₅L]ⁿ⁺ are the same, it can be concluded that the total complex charge is a factor that can influence the NMR chemical shifts of protons in the ligand.

If the positive charge is a major factor which could affect the chemical shift of the ligand, it is expected that the chemical shift of C_{(2)-H} for *cis*- [Co(en)₂(N-mIm) OPO₃H_x]^{x+} (x = 0, 1, 2) obeys the following order:



However, the experimental results show that the trends for the chemical shift of these complexes are reverse and have the following order:



As the molecular model shows (Figure), an intramolecular interaction between the phosphate anion group and the C_{(2)-H} of imidazole ring, which exists at pH higher than 9.00, has been proposed to account for this unexpected phenomenon. One can also conclude that the deshielding of C_{(2)-H} at pH higher than 9.00 could be related to this interaction. The chemical shifts of other protons, which are shown in the Table, do not change with pH.

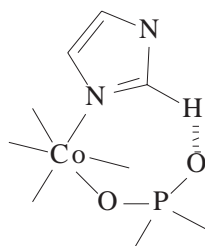


Figure. Molecular model of [Co(en)₂(N-mIm) OPO₃]⁰.

More interestingly, the chemical shift of C_{(2)-H} in *cis*- [Co(en)₂(N-mIm) OPO₃H_x]^{x+} (x = 0, 1, 2) compared to that of [(NH₃)₅CoImCo(NH₃)₅]⁵⁺ with a 5 positive charge is shifted downfield. This also may be assumed to a possible interaction between the phosphate anion group and the C_{(2)-H} of the imidazole ring in *cis*- [Co(en)₂(N-mIm) OPO₃H_x]^{x+}.

References

1. D. K. Lavalley and E.B. Fleischer, **J. Am. Chem. Soc.**, **94**, 2583-99 (1972).
2. R.J. Pugmire and D.M. Grant, **ibid**, **90**, 697-706 (1968).
3. R.J. Pugmire and D.M. Grant, **ibid**, **90**, 4232-8 (1968).
4. R.D. Foust and C.P. Ford, **ibid**, **94**, 5686-96 (1972).

5. M.F Hoqq and R.E. Shepherd, **Inorg. Chem**, **23**, 1851-58 (1984).
6. D.K. Lavalley, M.D. Baughman and M.P. Phillips, **J. Am. Chem. Soc**, **99**, 718-24 (1977).
7. C.R Clark, A.G. Blackman, M.R. Grimmett and A. Mobinikhaledi, **Can. J. Chem**, **77**, 178-81 (1999).
8. W. Henderson, R.E. Shepherd and J. Abola, **Inorg. Chem**, **25**, 3157-63 (1986).
9. A.G. Blackman, D.A. Buckingham, C.R. Clark and J. Simpson, **J. Chem. Soc. Dalton. Trans**, 3031-41(1991).
10. J.M. Malin, C.F. Schmidt and H.E. Toma, **Inorg. Chem**, **14**, 2924-28 (1975).
11. J.E. Figard, J.V. Paukstelis, E.F. Byrne and J.D. Petersen, **J. Am. Chem. Soc**, **99**, 8417-25 (1997).
12. C.R. Johnson, W.W. Henderson and R.E. Shepherd, **Inorg. Chem**, **23**, 2754-63 (1984).