**PMR & \(^{13}\)CMR Spectra of Some Imidazole Complexes of Cobaloximes**

**JAYANTA K DAS & KAILASH C DASH**
Department of Chemistry, Utkal University, Vanavihar, Bhubaneswar 751 004

Received 22 August 1984; revised and accepted 11 March 1985

Imidazole (Im) and its 1- and 2-substituted derivatives react with cobalt(II) chloride and dimethylglyoxime (DH\(_2\)) in presence of air to form cobaloxime complexes of the type \(\text{trans-}[\text{Co(DH)}_2(\text{Im})(\text{Cl})]\).

The \(^1\)H NMR (PMR) and the \(^{13}\)C NMR (CMR) spectra of four of these complexes and of imidazole and free DH\(_2\) ligand have been studied in DMF medium by Fourier Transform technique.

Cobaloximes are complexes containing the Co(DH\(_2\))\(^+\) moiety, where DH is the monoanion of dimethylglyoxime. They are known to simulate closely the reactions of vitamin B\(_{12}\) (refs. 2, 3) and have become leading models in the field of vitamin B\(_{12}\) chemistry. The five-membered heterocyclic ligand, imidazole, is present in many biological systems (e.g. in the histidyl residues of proteins) and provides a potential binding site for metal ions.\(^4,5\) The biological significance of cobaloximes and imidazoles prompted us to synthesise imidazole complexes of cobaloximes of the type \(\text{trans-}[\text{Co(DH)}_2(\text{Im})(\text{Cl})]\).

Keeping this in view, we have synthesised the cobaloximes and studied their \(^1\)H and \(^{13}\)C NMR spectra.

**Synthesis of complexes**

The complexes were synthesised from CoCl\(_2\).6H\(_2\)O, dimethyl glyoxime (DH\(_2\)) and the imidazole ligand and characterised by elemental analyses, electronic and IR spectra as well as conductivity measurements in non-aqueous medium.\(^6\)

**\(^1\)H NMR (PMR) spectra**

The \(^1\)H NMR spectra of imidazole, dimethylglyoxime and the complexes were recorded in DMF with TMS as the external reference on a Varian FT-80A spectrometer operating in Fourier mode using 5 mm insert tubes at a spin rate of 20 rps.

**\(^{13}\)C NMR (CMR) spectra**

Full spectral width (6000 Hz) random-noise \(^1\)H-decoupled 25 MHz \(^{13}\)C NMR spectra were recorded on the JEOL FX-100 instrument using the Fourier Transform technique which allows measurement of samples with \(^{13}\)C in natural abundance (1.1\%). The solvent was DMF and the spectra were recorded at ambient temperature. TMS served as the internal standard.

The assignment of ligand signals was made considering the literature values, the difference in intensity based on the Nuclear Overhauser Effect (NOE) and trends in the shifts.

We have earlier reported\(^6\) the synthesis, conductivity data, electronic and IR spectra and thermoanalytical data of a series of six-coordinated, diamagnetic and pseudo-octahedral cobalt(III) complexes of the type \(\text{trans-}[\text{Co(DH)}_2(\text{Im})(\text{Cl})]\). The NMR spectra offer great help in elucidating the stereochemistry, as the two possible conformations, i.e. the cis and trans are expected to show different resonances, and as the effect of variation of one ligand on the NMR spectra of other ligands can be studied.\(^8\)

The PMR shifts (values in \(\delta\), ppm) of the chlorocobaloxime complexes (structure III) clearly show (Table I) that on coordination the signal due to CH\(_3\) group of DH\(_2\) (structure I) at 1.98 undergoes a clear downfield shift by about 0.4 to 2.36-2.38. In all the complexes this signal appears as a very sharp singlet indicating the presence of only one CH\(_3\) signal in solution.
The imidazole protons also undergo a considerable downfield shift. On coordination to cobalt(III) centre the equivalence of H-4 and H-5 (structure II) in imidazole is lost and separate signals appear, and further, the electron withdrawal by central cobalt(III) leads to a marked deshielding of the protons adjacent to the pyridine nitrogen (N-W3)11. The situation is indeed parallel to that observed on protonation of a neutral, unsubstituted imidazole species relative to a non-protonated species12-13. The H-2 signal is seen in 1-substituted imidazoles at 7.4, shifted downfield by about 0.4 from the free ligand value. The H-4 and H-5 in complexes appear around 7.3 and 6.9 respectively. The signals due to various 1- and 2-substituents have been also assigned.

The $^{13}$C NMR signals of the imidazole ligands also undergo a downfield shift on complexation and C-4 and C-5 now resonate at different fields. The C-2, C-4 and C-5 of the imidazole ring resonate at 138, 127 and 122 respectively. The substituents at 1- and 2-positions of the imidazole ring have also been appropriately assigned.

The results of this investigation establish a clear trans-structure for the imidazole complexes of the chlorocobaloximes [Co(DH)$_2$(Im)(Cl)]. The coordination to cobalt(III) centre the equivalence of H-4 and H-5 (structure II) in imidazole is lost and separate signals appear, and further, the electron withdrawal by central cobalt(III) leads to a marked deshielding of the protons adjacent to the pyridine nitrogen (N-W3)11. The situation is indeed parallel to that observed on protonation of a neutral, unsubstituted imidazole species relative to a non-protonated species12-13. The H-2 signal is seen in 1-substituted imidazoles at 7.4, shifted downfield by about 0.4 from the free ligand value. The H-4 and H-5 in complexes appear around 7.3 and 6.9 respectively. The signals due to various 1- and 2-substituents have been also assigned.

The $^{13}$C NMR spectra also show some striking changes in the $^{13}$C NMR spectra also. The oxime CH$_3$ carbon is considerably shifted downfield on coordination and appears invariably as a very sharp signal at 12.4 in all the complexes. The imine carbon appears around 152 uniformly, which is slightly upfield compared to the value for free DH$_2$. The $^{13}$C NMR spectra of the imidazole ligands also undergo a downfield shift on complexation with cobalt(III) and appear at different fields. The C-2, C-4 and C-5 of the imidazole ring resonate at 138, 127 and 122 respectively. The substituents at 1- and 2-positions of the imidazole ring have also been appropriately assigned.

The results of this investigation establish clear trans-structure for the imidazole complexes of the chlorocobaloximes [Co(DH)$_2$(Im)(Cl)].
nation of both ligands has been firmly established and further it is shown that the imidazole derivatives are bonded to the metal atom through the pyridine nitrogen (N-3). The probability of the presence of any other distinct chemical species in solution is also ruled out. Since cobalt(III) can be introduced into a variety of metalloprotein, the results are expected to provide a model not only for the cobalt(III) derivatives, but also for the closely related zinc(II) systems14-15.

The authors are indebted to Prof. A. Schmidpeter, Munich University, Munich for his ungrudging help in getting the FT NMR recorded. One of the authors (JKD) thanks the UGC, New Delhi for a Teacher Fellowship and the Government of Orissa for leave of absence.

References
1 Schrauzer G N. Acc chem Res. 1 (1968) 97.
6 Das J K & Dash K C. Proc natl Acad Sciences, India. (accepted).
7 Fay R C & Piper T S. J Am chem Soc. 84 (1962) 2303.
12 Pugmire R J & Grant D M. J Am chem Soc. 90 (1968) 4232.