

**IZOMERISATION MECHANISMS OF STEREOLABILE TRIS- and BIS- BIDENTATE
OCTAHEDRAL COBALT (II) COMPLEXES: X-RAY STRUCTURE AND VARIABLE
TEMPERATURE(VT) AND VARIABLE PRESSURE(VP) NMR KINETIC INVESTIGATIONS**

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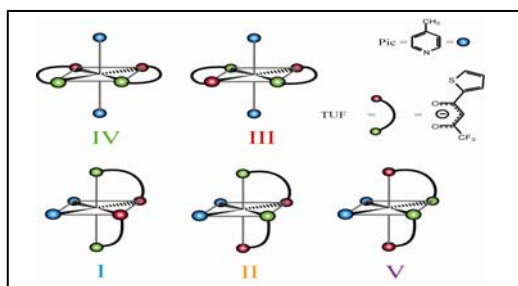
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The understanding of isomerization processes in labile divalent 3d-metal complexes are still open to many questions. Though dynamic NMR spectroscopy in the conditions of VT and VP is a well-known tool to investigate rather inert complexes, it has also been successfully employed in stereochemical studies of labile cobalt(II) complexes in solution. Providing that the electron spin relaxation is at its optimum, NMR spectroscopy can be used to investigate equilibria and kinetics of isomeric forms of paramagnetic complexes in solution. It has been established that the dipolar pseudocontact component is the predominant factor for paramagnetic NMR chemical shift in Co(II) ($^4T_{1g}$) coordination compounds.

Octahedral cobalt (II) complexes usually undergo substitution reactions according to dissociative pathways. By analogy, two isomerization patterns involving only single step dissociative mechanisms (pentacoordinated trigonal bipyramidal intermediate) can be suggested:

Monodentate dissociative mechanism: dis-sociative Pic bound/free ligand exchange may proceed with isomerization, or not. Bidentate bond-rupture mechanism: it involves the breaking of the weakest Co–O bond with the TUF ligand (closest to the CF₃ withdrawing group). The reformation of the bond may lead to



isomerization, or not. This mechanism is not purely dissociative, since TUF remains partially bonded to the metal centre in the intermediate. Hence this is a bond-rupture mechanism.

It can be shown that among the ten possible isomerization reactions, only six can directly occur for a single step dissociative mechanism. These six possible routes are shown.

Among those six routes, four ($\text{II} \rightleftharpoons \text{IV}$, $\text{II} \rightleftharpoons \text{I}$, $\text{II} \rightleftharpoons \text{V}$, $\text{II} \rightleftharpoons \text{IV}$ & $\text{III} \rightleftharpoons \text{V}$) are common for both isomerization patterns suggested above. However the route $\text{I} \rightleftharpoons \text{III}$ can occur for the monodentate dissociative mechanism but not for the

bidentate bond-rupture mechanism. In contrary, the route $\text{III} \rightleftharpoons \text{IV}$ can occur for the bidentate case but not for the monodentate one. Over the whole range of temperature studied, a very good agreement between experimental and fitted data was obtained when the route $\text{I} \rightleftharpoons \text{III}$ was neglected (see the excellent agreement between experimental and calculated spectra), while neglecting $\text{III} \rightleftharpoons \text{IV}$ did not lead to an acceptable fit of the spectra. On the basis on these observations, the bond rupture mechanism is suggested for the isomerization of compound **1** in CD₂Cl₂. The five possible isomers of the octahedral adduct [Co(TUF)₂(Pic)₂] were observed and identified by ¹⁹F NMR, in CD₂Cl₂. The thermodynamic parameters (ΔH° , ΔS°) between all the isomers for the isomerization equilibria were determined. The lineshape analysis of the spectra allowed to identify the isomerization pathways. Among the two possible single step dissociative mechanisms, the bidentate single bond rupture gave the most satisfying fit over the whole temperature range.