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VARIABLE PRESSURE (VP) AND VARIABLE TEMPERATURE (VT) ^{19}F NMR INVESTIGATION OF MOLECULAR EXCHANGE MECHANISMS IN OCTAHEDRAL COBALT(II) COMPLEXES

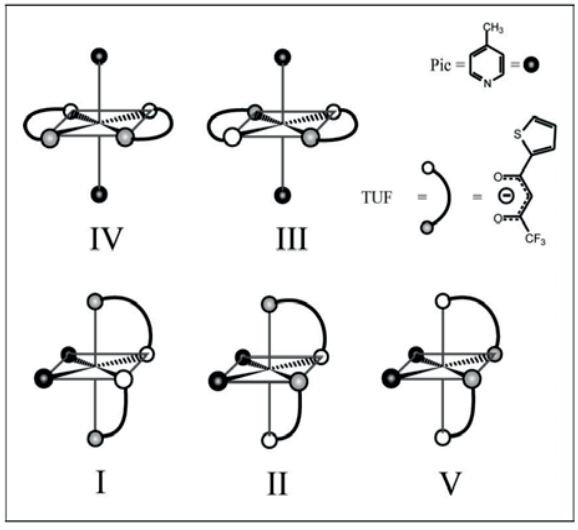
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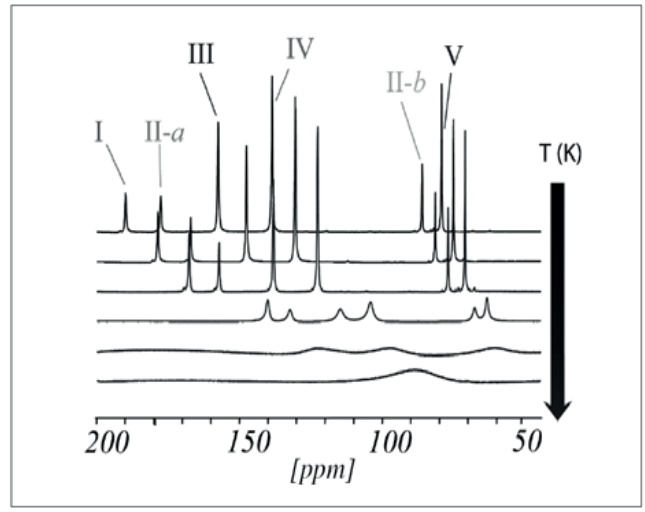
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The labile cobalt(II) complex $[Co(TUF)_2(Pic)_2]$ with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TUF) bidentate and 4-methylpyridine (Pic) monodentate ligands was studied by variable temperature (VT) and variable pressure (VP) ^{19}F NMR. In contrast to the solid state, all the isomers are present in a CD_2Cl_2 solution. Thermodynamic parameters (ΔH^0, ΔS^0 and ΔV^0) of each isomer with reference to the *trans*(N)-*trans*(CF3)-*trans* isomer were obtained from the fitting of experimental mole fraction values.



Schematic representation of the five isomers of $[Co(TUF)_2(Pic)_2$



Evolution of the ^{19}F NMR signals of the five isomers of $[Co(TUF)_2(Pic)_2]$ with increasing temperature.

A kinetics investigation of the isomerization processes was performed by lineshape analysis of the spectra using the Kubo-Sack formalism. The suggested bidentate bondrupture mechanism involves the breaking of the weakest Co–O bond (closest to the CF_3 withdrawing group) with the TUF ligand.

Heterometallic μ_3-oxo carboxylate complexes (Fe_2Co and Fe_2Ni) have been studied by 2D NMR. The magnetic properties of these compounds are compared in the solid state and in the liquid state.