cis–trans-Isomerism in Solution for the Tris-(*N*-*p*-tolylpyridinaldimine)cobalt(II) Cation

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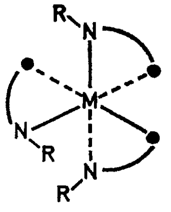
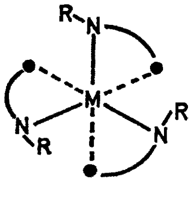
Summary *cis–trans*-geometrical isomerism in solution for the tris-(*N*-*p*-tolylpyridinaldimine)cobalt(II) cation has been detected and investigated as a function of temperature by ^{1}H n.m.r.

Although tris-complexes containing identical but unsymmetrical ligands may exist as either *cis*- or *trans*-geometrical isomers, ^{1}H n.m.r. studies on the related tris-*N*-R-salicylaldimine,[1] *N*-R-keto-imine,[2] *N*-R-pyrrolaldimine,[1,2] and *N*-R-2-hydroxyacetophenimine[3] complexes of $\mathrm{V^{III}}$ and $\mathrm{Co^{III}}$ have detected only the *trans*-configuration (A). For the idealized *cis*-isomer (B) with a C_3 symmetry axis, only one proton resonance is expected for each ligand position, while for the *trans*-form (A), owing to a lack of symmetry, three separate signals of equal intensity are expected for each chelate ring substituent. The pronounced deviation from the statistically predicted *cis* : *trans* ratio of 1 : 3 for these tris-(*N*-R-substituted) imine complexes has led to the speculation that the factor governing the final *cis–trans*-isomer distribution is the unfavourable steric "crowding" accompanying formation of the *cis*-form (B),[4] in which all three R groups are forced to occupy the same octahedral face. While it can be argued that this steric consideration may well be influential, the detection by ^{1}H n.m.r. of both



(A) *trans*



(B) *cis*

cis- and *trans*-isomeric forms for the tris-(*N*-*p*-tolylpyridinaldimine)cobalt (II) cation [hereafter $Co(pti)_3^{2+}$, Figure] establishes that such steric requirements do not exclusively determine the final isomer populations. The *cis*-geometrical configuration has been reported for those cases in which the bidentate ligands have the same donor atoms (β-diketonates[5,6]) or sterically similar donor groups (amino-acids[7] and β-thioketonates).[8]

The ^1H n.m.r. spectrum of the $Co(pti)_3(BPh_4)_2$ salt dissolved in CD_2Cl_2 is shown in the Figure. Ligand proton assignments for the pyridine fragment have been made by analogy with the previous reported spectrum of tris-(2,2′-bipyridyl)cobalt(II)[9] while the phenyl *para*-CH_3, *ortho*-H, and *meta*-H resonance positions have been established by R group substitution *i.e.* R = methyl, phenyl. Although most of the $Co(pti)_3^{2+}$ proton signals show some multiplicity, the four upfield *ortho*-H resonances provide unmistakeable evidence for the presence of a *cis–trans*-isomer mixture in solution. The three equally intense signals at +54·4, +36·4, and +29·8 p.p.m. from internal Me_4Si undoubtedly characterize the *trans*-form, while the single, less intense peak at +21·6 p.p.m. is attributable to the *cis*-isomer.

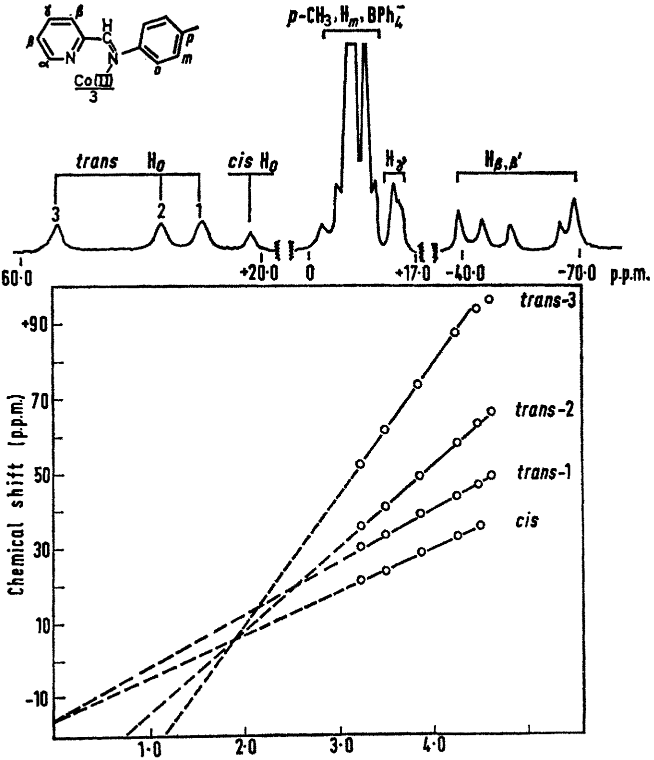


FIGURE. ^1H *n.m.r. trace of* $Co(pti)_3(BPh_4)_2$ *in* CD_2Cl_2 *at* 26° *from internal* Me_4Si *and temperature dependence of the* cis- *and* trans-*isomer* ortho-H (H_0) *resonances. The broad downfield pyridine* H_α (ca. −85 and −140 p.p.m.) *and methine proton* ca. −235 p.p.m.) *resonances are not shown.*

The temperature dependence of the *cis*/*trans* isomer ratio, as determined from the integrated intensities of the *ortho*-H signals, demonstrates the presence of a solution

$$trans\text{-}Co(pti)_3^{2+} \rightleftarrows cis\text{-}Co(pti)_3^{2+}$$

equilibrium. At 26° (Figure), the *cis*/*trans* ratio is considerably less than the statistically predicted value of 0·33, although the experimental value of 0·17 is perhaps surprisingly large in view of the rather sizeable steric requirement of a *p*-tolyl substituent. As the temperature is decreased, the *cis*/*trans* isomer ratio tends to zero until at *ca.* −60° only the three *ortho*-H resonances due to the *trans*-isomer are still observed. A decrease in the *cis*-isomer concentration which parallels the decrease in temperature has been reported for tris-complexes of unsymmetrical β-diketones[5] and is in agreement with the expected lower thermodynamic stability of the *cis*-isomeric form. Furthermore, the *cis*/*trans* ratio is also found to be solvent dependent with the percentage of the *cis*-form at 26° decreasing gradually according to the sequence: CD_2Cl_2 (0·17) > CD_3CN (0·13) > $(CD_3)_2CO$ (0·10).

The temperature dependence of the *ortho*-proton resonances for both the *cis*- and *trans*-isomers are also shown graphically in the Figure. Since the contact shift interactions for all the *ortho*-protons are expected to be approximately equal, the observed, well-separated signals allowing unambiguous detection and assignment of the *cis*- and *trans*-geometric isomers are attributed to differences in dipolar shift contributions. Thus for the $Co(pti)_3^{2+}$ *trans*-isomer, each of the three non-equivalent *ortho*-protons (spinning phenyl rings) experiences different dipolar shifts which are in turn different from the dipolar shifts for the three equivalent *ortho*-H protons in the trigonally symmetric *cis*-isomer. The magnitude of these dipolar shift interactions undoubtedly contributes to the observed upfield shifts according to the sequence, *cis* < *trans*-1 < *trans*-2 < *trans*-3.

While each of the *ortho*-H resonances in the Figure gives approximately a straight line in the temperature range investigated, none of them exhibits simple Curie-law behaviour in that the chemical shifts decrease *faster* than predicted as the temperature is lowered. Furthermore, the degree of deviation is found to exactly parallel the increase in dipolar shift contribution: *cis* < *trans*-1 < *trans*-2 < *trans*-3. Presumably the anomalous Curie behaviour of the observed shifts is primarily due to a non-Curie behaviour of the dipolar components[10] of the *ortho*-H phenyl isotropic shifts.

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