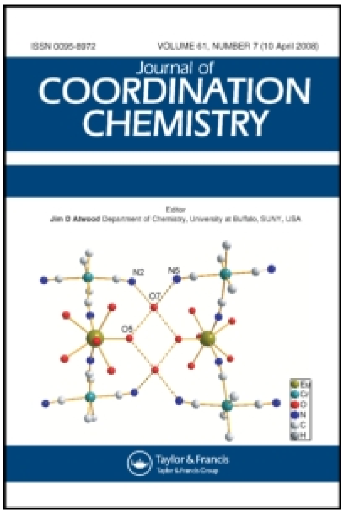

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NMR DETECTION OF CIS AND TRANS ISOMERS OF PSEUDOOCTAHEDRAL METAL(II) COMPLEXES WITH THE UNSYMMETRICAL BIDENTATE LIGANDS N-R-PYRIDINALDIMINES

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NMR DETECTION OF CIS AND TRANS ISOMERS OF PSEUDOOCTAHEDRAL METAL(II) COMPLEXES WITH THE UNSYMMETRICAL BIDENTATE LIGANDS N-R-PYRIDINALDIMINES[1]

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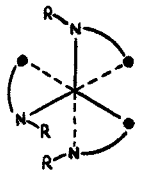
Proton magnetic resonance spectra of solutions of six-coordinated M(N–R-pyridinaldimine)$(PF_6)_2$ complexes (M = Fe(II), Co(II), Ni(II) and Zn(II)) show the presence of both *cis* and *trans* isomers in equilibrium. Cobalt(II) complexes are the most suitable for detection of this type of isomerism. The *cis–trans* isomer distribution has been found to be dependent on the bulkiness of R, on the solvent, on temperature, and on the charge, if present, on the ligand.

INTRODUCTION

It is well known that six-coordinated metal complexes formed with three unsymmetric bidentate ligand molecules may exist as *cis* and *trans* isomers of the type shown below.[3]



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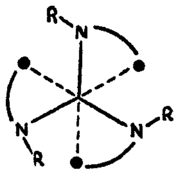
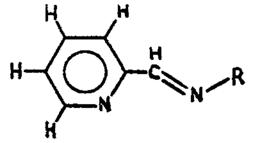


Cis

Since the nmr technique has been applied to the detection of these isomers some information has been obtained on the existence and on the thermodynamic stability of these isomers.[4–8] Detection rests on the fact that for the idealized *cis* isomer with a C_3 symmetry axis only one resonance is expected for each set of equivalent ligand protons while for the *trans* form, owing to the lack of symmetry, three separate signals are expected. However the research until now has been limited on cobalt(III) and vanadium(III) complexes with anionic ligands.[4] In order to establish the effects of the steric requirements and of the charge of the ligands on the *cis–trans* isomer distribution we have performed an nmr investigation on cobalt(II), nickel(II), iron(II), and zinc(II) complexes with the asymmetric bidentate ligands formed from pyridin-2-aldehyde and various amines.



R = methyl (PMI), ethyl (PEI), *i*-propyl (P*i*PI), phenyl (PAI), *p*-tolyl (PTI).

These complexes were found to be six-coordinated.[9] They have been prepared as PF_6 salts in order to increase their solubility in acetone and acetonitrile.

EXPERIMENTAL

Preparation of the Complexes

All of the complexes were prepared by the same general method. A CH_3OH solution of the $MCl_2 \cdot 6H_2O$ salt (2 mmoles) was added to a boiled solution of pyridine-2-aldehyde and the appropriate amine. By adding 4 mmoles of KPF_6 dissolved in 30 ml H_2O to the above solution, and upon cooling, crystals were obtained. The compounds were recrystallized from acetone-ether solutions. Their analyses are reported in Table I.

Proton Magnetic Resonance Spectra

Pmr spectra were obtained on a Varian DA-60 spectrometer operating at 60 Mc using d_3-acetonitrile and d_6-acetone solutions with tetramethylsilane (TMS) as an internal reference. Unless otherwise specified, the spectra were measured at 26° C. For the diamagnetic iron and zinc complexes, proton

TABLE I

Analytical data for the complexes

Compound	Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
$Fe(PMI)_3(PF_6)_2$	35.70	3.42	11.89	36.02	3.45	12.10
$Fe(PTI)_3(PF_6)_2$	50.12	3.88	8.99	49.95	4.06	8.97
$Zn(PMI)_3(PF_6)_2$	35.23	3.37	11.74	35.58	3.57	11.92
$Co(PMI)_3(PF_6)_2$	35.56	3.41	11.85	35.95	3.54	12.08
$Co(PEI)_3(PF_6)_2$	38.36	4.02	11.19	38.50	3.95	11.28
$Co(P\textit{i}PI)_3(PF_6)_2$	40.82	4.57	10.59	40.15	4.49	10.59
$Co(PAI)_3(PF_6)_2$	48.28	3.38	9.38	47.90	3.23	9.20
$Ni(PAI)_3(PF_6)_2$	48.28	3.38	9.38	47.91	3.54	9.22
$Ni(PTI)_3(PF_6)_2$	49.96	3.87	8.96	49.61	3.80	9.01

resonance positions were obtained operating in internal lock, whereas for the paramagnetic nickel and cobalt complexes, resonance frequencies were measured in the HR mode using the conventional side band calibration technique.

RESULTS

Iron(II) and Zinc(II) Complexes

Typical pmr traces of the two diamagnetic complexes are reported in Figure 1. The iron(II) derivative with R=CH_3 shows four distinct doublets in the region of the NCH_3 resonances. Three of them are equally intense and the fourth is less intense. The latter peak is unmistakably attributed to the *cis* form whereas the former peaks are due to the *trans* isomer. The *p*-tolyl derivative, however, shows only two *p*-CH_3 peaks (at −2.00 and 2.04 ppm from TMS) differing slightly in intensity. This means that the expected four signals are pairwise degenerate.

The R=CH_3 zinc complex shows only one CH_3 peak at 26° C. At −25° C splitting into two signals occurs. Their relative intensity is solvent dependent, i.e. a larger difference is observed in acetone than in acetonitrile (see Figure 1).

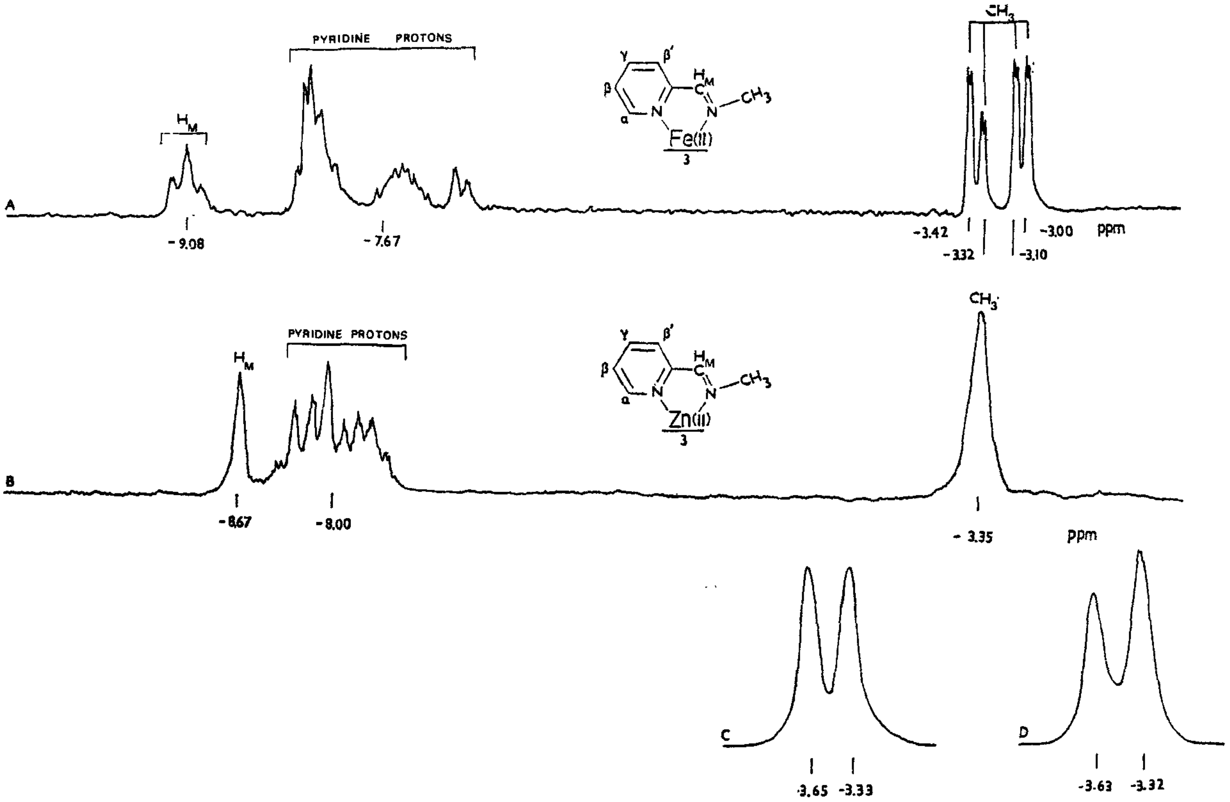


FIGURE 1 Pmr spectra in d_3-acetonitrile at 26° from internal TMS od $Fe(PMI)_3^{2+}$ (A) and $Zn(PMI)_3^{2+}$ (B). At the bottom from the left the splitting of the N—CH_3 resonance of the latter compound at −25° in d_3-acetonitrile and d_6-acetone.

Cobalt(II) and Nickel(II) Complexes

In Figure 2 a complete spectrum of the *N*-methyl derivative in d_3-acetonitrile is shown. Four N—CH$_3$ and three (of intensity close to 1 : 1 : 2) *ortho* and azomethinic hydrogen peaks are clearly indicative of a *cis–trans* isomer distribution. This is further confirmed by the *N*-ethyl and *N*-phenyl derivatives reported in the same figure. For the *N*-ethyl derivative both the d_3-acetonitrile (right) and d_6-acetone (left) spectra are shown.

For the N-*i*-propyl complex (Figure 3) eight peaks attributed to the CH$_3$ protons are present, i.e. twice as many as for the previous derivatives. This is presumably due to the lack of free rotation of the *i*-propyl group which renders the two methyls non-equivalent. The trace at the top of Figure 3 shows the spectrum in acetonitrile whereas the one at the bottom shows the spectrum in acetone.

The nickel complexes give rise to very broad peaks with consequent poor resolution (see Figure 4). The *N*-phenyl derivative shows two *para*-proton resonances of intensity ≃ 1 : 1.6. If the intensity ratio were 1 : 1, it would be indicative of a statistical *cis–trans* isomer distribution, whereas a 1 : 2 ratio would be indicative of only the *trans* isomer. The *P*-tolyl derivative shows three equally intense *p*-CH$_3$ peaks due only to the *trans* form. A fourth peak may be masked by the broad and intense peak due to the *meta* and γ protons.

DISCUSSION

Although all the spectra strongly indicate the

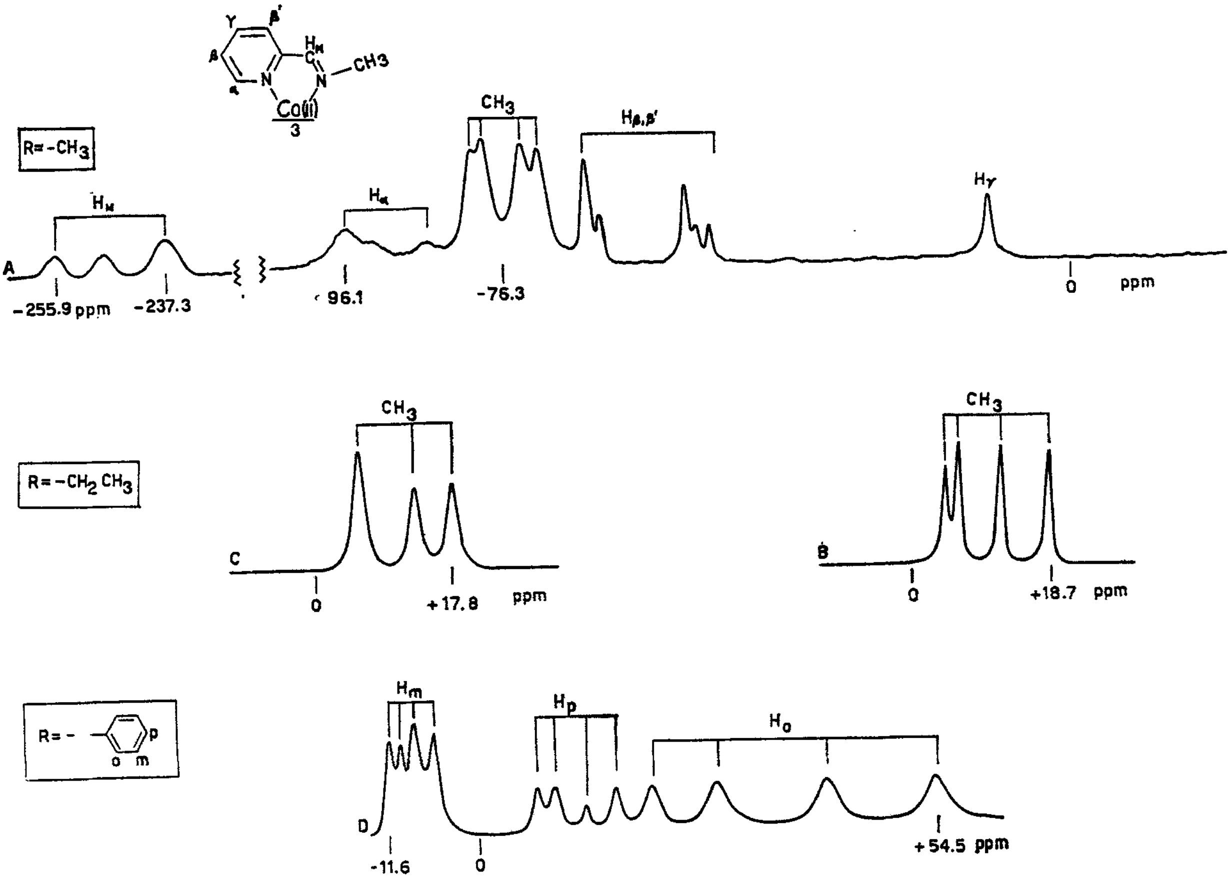


FIGURE 2 Pmr spectra at 26° from internal TMS of Co(PMI)$_3^{2+}$ in d_3-acetonitrile (A), Co(PEI)$_3^{2+}$ in d_3-acetonitrile (B) and d_6-acetone (C), Co(PAI)$_3^{2+}$ in d_3-acetonitrile (D).

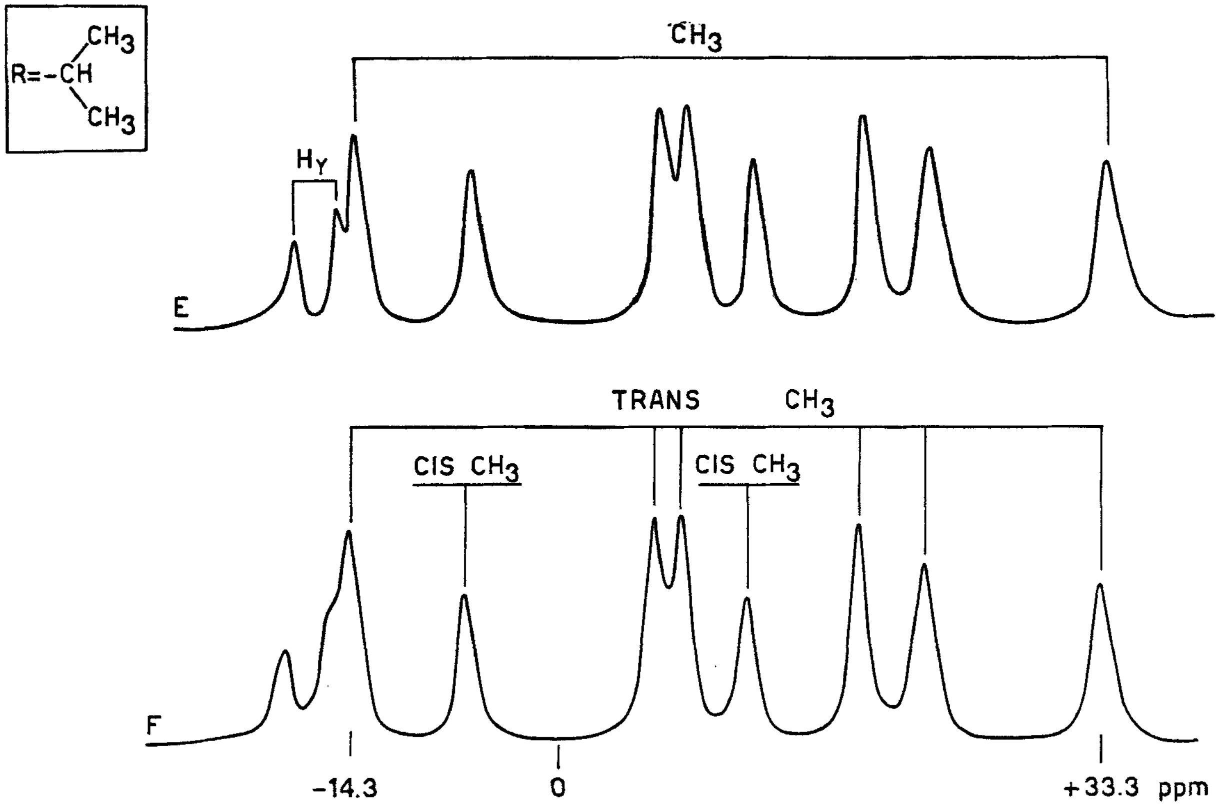


FIGURE 3 Pmr spectra at 26° from internal TMS of theCo(P*i*PI)$_3^{2+}$ complex in d_3-acetonitrile (top) and d_6-acetone (bottom).

presence of *cis* and *trans* isomers, there is a large difference among the various metals in allowing clear isomer detection by the nmr technique. In the diamagnetic iron(II) complexes, the NCH_3 group is the most sensitive in detecting the presence of the isomers. This is presumably due to the proximity of this group to the central metal ion. In fact the *p*-tolyl derivative of iron(II) shows only two CH_3 signals.

For the zinc complex the presence of only one signal at room temperature is due to the lability of six-coordinated zinc(II) complexes. On the nmr time scale rapid ligand exchange or *cis–trans* equilibrium accounts for the observed spectrum.[10] By decreasing the temperature down to $< -20°$ C, the rate of such interconversions goes down so that a splitting of the signals (still pairwise degenerate) is observed.

But the most clear isomer detection occurs in the spectra of the cobalt complexes. This is due to favorable electronic relaxation times which are responsible for the sharpness of the signals relative to the large shift range characteristic of paramagnetic molecules. Moreover the large contribution of dipolar shifts to the total chemical shifts, general in pseudooctahedral cobalt(II) complexes,[11–16] causes the large non-equivalence between the *cis* and *trans* isomers and among the three ligand molecules themselves in the *trans* form. It is known that the dipolar shifts depend on the anisotropy of the *g* factor components and on the geometric coordinates of the resonating protons.[13] *Cis* and *trans* isomers will have different anisotropic properties, i.e. two *g* components for the *cis* form and three for the *trans* one. The different coordinates of the ligand protons in the *trans* isomer are responsible for the large splitting observed.[14, 15]

In pseudooctahedral nickel complexes electronic relaxation times are not favorable, thus the peaks are broad. Moreover, in the absence of detectable dipolar shift contributions,[13] the non equivalence

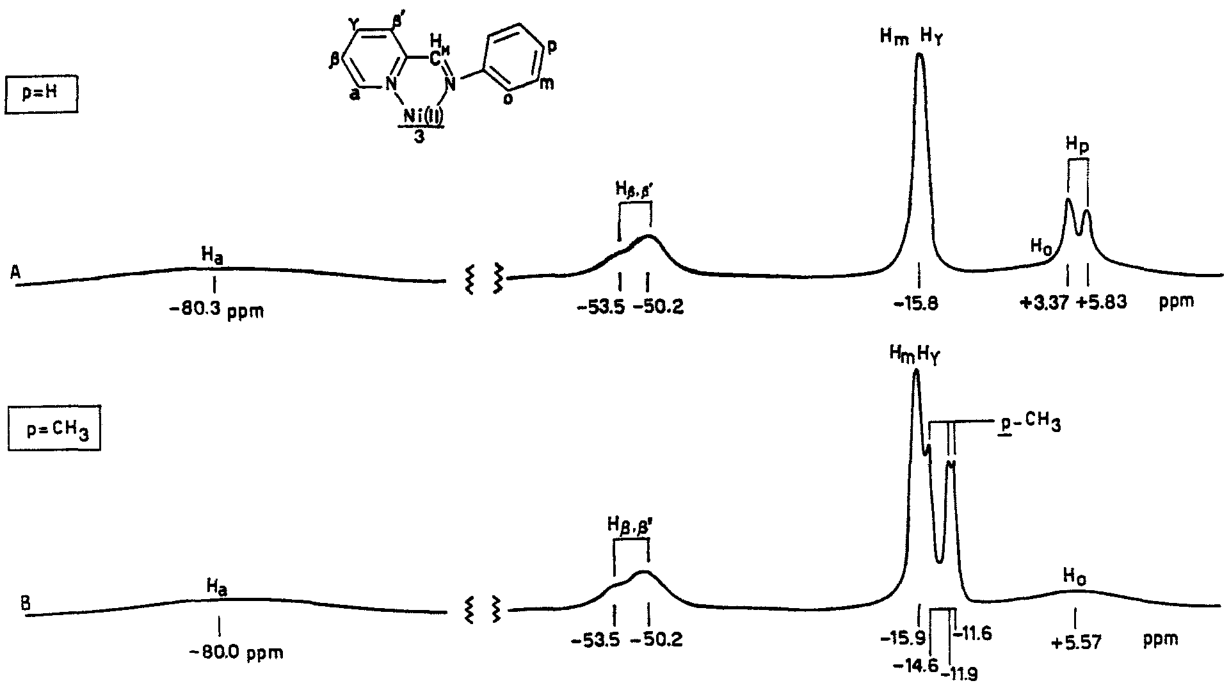


FIGURE 4 Pmr spectra at 26° from internal TMS of $Ni(PAI)_3^{2+}$ (top) and $Ni(PTI)_3^{2+}$ in d_3-acetonitrile.

of the protons have not been magnified. Therefore the spectra are of little use in detecting the presence of isomers.

From the reported spectra it can be shown that the solvent is an important factor in determining the final *cis–trans* isomer population. Acetonitrile in general stabilizes the *cis* isomer with respect to acetone. In Table II an estimation of the percentage of the *cis* isomer present in solution is reported. The solvent dependence of the peak intensities together with their temperature dependence (i.e. the intensity of the *cis* peak always decreases with temperature[14]) demonstrate the presence of *cis–trans* solution equilibria. The influence of the central metal ion on the equilibrium constant is probably due only to the metal donor distances which determine the steric repulsions among the ligands in the two forms. They should vary in the order: Fe(II) (low spin) < Co(II) ≃ Ni(II) < Zn(II).[17] The *cis–trans* isomer equilibrium is strongly affected by the bulkiness of R in the order: methyl < ethyl < *i*-propyl (non-spinning) < phenyl (spinning). This factor had previously been considered,[4] however the steric requirements of the ligands apparently do not exclusively determine the isomer population. In fact tris(N-R-pyrrolaldiminate)cobalt(III) complexes have been found to be only *trans*,[18] although the ligands are sterically very similar to the present pyridinaldimines except for the charge. Probably the electrostatic repulsions of three charged atoms on the very same face of the octahedron play an important role in destabilizing the *cis* isomer. Furthermore, among the various imines investigated (β-ketoimines,[19] salicylaldi-

TABLE II

[*Cis*]/[*trans*] isomer ratios for the tris(N–R–pyridinaldimine) metal(II) hexafluorophosphate salts[a]

Complex	*R* group	[*cis*]/[*trans*] isomer ratio[b,c] acetonitrile-d_3	acetone-d_6
$Fe(PMI)_3^{2+}$	CH_3	0.20	0.16
$Zn(PMI)_3^{2+}$	CH_3	0.33[d]	0.27[d]
$Co(PMI)_3^{2+}$	CH_3	0.33	0.28
$Co(PEI)_3^{2+}$	CH_2CH_3	0.30	0.15
$Co(PiPI)_3^{2+}$	$CH(CH_3)_2$	0.26	0.22
$Co(PAI)_3^{2+}$	C_6H_5	0.12	0.09

[a] At 26° C except when specified.
[b] Statistical [*cis*]/[*trans*] ratio is 0.33.
[c] All values are an average of at least six integrations (estimated error ± 0.01).
[d] Determined at −28° C.

mines,[18] and 2-hydroxyacetophenimine[20]) only the present neutral pyridinaldimines give rise to an appreciable amount of *cis* form even when *R* is as large as a rotating (around the N—C bond) phenyl.

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