Trifluoroacetate Complexes of Cobalt(II), Nickel(II), and Copper(II) with Pyridine-type Ligands. Part III.[1] Nuclear Magnetic Resonance Studies of Cobalt(II) Complexes in Solution

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Complexes of cobalt(II) trifluoroacetate with pyridine and alkylpyridine ligands of stoicheiometries ML_4T_2 and ML_2T_2 have been investigated in solution by ^1H and ^{19}F n.m.r. spectroscopy. In deuteriochloroform solution, *cis–trans* isomeric equilibria were detected for both series of complexes. Rapid *cis–trans* exchange occurred at ambient temperatures but became slow on the n.m.r. time scale below *ca.* 0 °C for ML_2T_2 complexes and below *ca.* −50 °C for ML_4T_2 complexes. In the ML_4T_2 series, intermediate species were detected between *ca.* 0 °C and *ca.* −40 °C. In hexadeuterioacetone solution, a number of polymeric species were detected. Some evidence has also been obtained for a rapid intramolecular scrambling of ligands occurring in these complexes even at temperatures below −60 °C.

EARLIER parts[1] of this work have described the details of preparation, thermal decomposition, and some studies of the stereochemical and structural properties of metal trifluoroacetate complexes with heterocyclic ligands (L). Electronic and vibrational spectroscopic techniques were shown to provide a useful but to some extent limited insight into the structures of these complexes whereas the present paper discusses the much more informative n.m.r. studies on the cobalt(II) complexes in solution.

Most of the Co^{II} complexes studied to date by n.m.r.[2] have been of stoicheiometry ML_4X_2 [3,4] where X = Cl, Br, I, NCS, for example, and L = py, alkylpy, or pyNO, ML_2X_2 [5-7] where X = acac, L = py, alkylpy, or pyNO, or ML_3^{2+} [8,9] where L = bipy, phen. In the first two series, no evidence was obtained for more than a single isomer (generally assumed the *trans*-isomer) in solutions containing an excess of free ligand. The only real evidence for *cis–trans* isomeric distinction in solutions of complexes has come from the ML_3^{2+} series where the bidentate ligand L was an unsymmetrically substituted bipy or phen molecule.[10] The present work describes n.m.r. studies on the complexes CoL_4T_2 and CoL_2T_2 where *cis–trans* isomeric distinction is clearly shown and where the temperature dependence of the rate of interconversion can be easily followed.

EXPERIMENTAL

The cobalt(II) complexes were prepared as previously described.[1] N.m.r. studies were performed on concentrated solutions of the complexes in deuteriochloroform (99·8% pure) and hexadeuterioacetone (99·5% pure). Preliminary 60 MHz ^1H n.m.r. studies and 56·458 MHz ^{19}F studies were made on a Perkin-Elmer R 10 spectrometer fitted with a standard variable temperature probe. A Digiac (Digico Ltd.) 4096 channel digital computer was used for c.a.t. experiments. The majority of the ^1H spectra were obtained using either a Varian HA 100 spectrometer or a JEOL MH 100 spectrometer, both operating at 100 MHz. In order to accommodate the large sweep-width required, the latter instrument had to be operated somewhat unconventionally. The technique involved allowing the magnetic field to drift in a controlled manner by introducing a small voltage to the input of the magnet flux stabiliser using the ' drift ' control on the magnet console. The sweep rate and direction were dependent on the magnitude and polarity of the input voltage, respectively. Spectra were recorded using either 1000 s or 2500 s sweep times which enabled sweep-widths of 120 p.p.m. or 300 p.p.m. respectively to be obtained within the standard chart length. The reproducibility of the spectra was very high but individual spectra were nevertheless calibrated using the separations of centre band and first lower side band absorptions, this separation being equal to the r.f. modulation frequency of 4 kHz.

All ^1H spectra were referenced internally to tetramethylsilane, isotropic shifts of the complexes being then calculated with respect to the shifts of the free ligand hydrogens (rel. to Me_4Si). ^{19}F Spectra were referenced relative to external trifluoroacetic acid. No bulk susceptibility corrections were made, these being considered negligibly small compared to the absolute magnitude of the shifts.

RESULTS AND DISCUSSION

Initial studies on solutions containing known amounts of complex and free ligand produced plots of observed shift against mole fraction of complexed ligand, as performed by Forster,[11] which were grossly non-linear. This implied that the observed shifts were not simply weighted averages of shifts due to a single diamagnetic and paramagnetic species but were being influenced by other factors such as intermolecular exchange effects (*e.g.* involving more than one paramagnetic or diamagnetic species) or perhaps intramolecular exchange processes (*e.g.* involving some type of structural rearrangement of the complex which involves additional averaging of hydrogen environments). It was thus

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[1] Part I, C. A. Agambar and K. G. Orrell, *J. Chem. Soc.* (*A*), 1969, 897; Part II, C. A. Agambar, P. Anstey, and K. G. Orrell, preceding paper.

[2] G. A. Webb, *Ann. Rep. of N.M.R. Spectroscopy*, 1970, **3**, 211, and references therein.

[3] D. Forster, *Inorg. Chem.*, 1973, **12**, 4; *Inorg. Chim. Acta*, 1971, **5**, 465; *ibid.*, 1968, **2**, 116.

[4] I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chim. Acta*, 1972, **6**, 185.

[5] R. W. Kluiber and W. De W. Horrocks, *J. Amer. Chem. Soc.*, 1965, **87**, 5350.

[6] E. E. Zaev and Y. N. Molin, *J. Struct. Chem.*, 1966, **7**, 639.

[7] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, 1963, **39**, 1211.

[8] I. Bertini and L. J. Wilson, *J. Chem. Soc.* (*A*), 1971, 489.

[9] M. L. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**, 2196.

[10] G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, 1970, **92**, 3021; *Inorg. Chem.*, 1970, **9**, 1546.

[11] D. Forster, K. Moedritzer, and J. R. Van Wazer, *Inorg. Chem.*, 1968, **7**, 1138.

necessary to establish the stoicheiometry of the complexes in solution. This was done by carefully measuring the relative intensities of bands due to free and complexed ligand hydrogens for solutions at *ca.* −40 °C containing accurately known amounts of free and complexed ligand. The results of such experiments are given in Table 1. The error associated with these measurements was quite large and the ligand : metal values are considered accurate only to ±0·5. It will, however, be observed that the values are approximately 4 and 2 for the L_4 and L_2 complexes, respectively, being somewhat low for the L_4 complexes and somewhat high for the L_2 series. This implies that there is an $L_4 \rightleftharpoons L_2$ equilibrium in solutions of $CDCl_3$ containing free ligand as has already been demonstrated by electronic spectroscopy.[1] The low ratios for the L_4 complexes are also due to the fact that, owing to solubility difficulties, only the more abundant isomeric L_4 species could be detected and included in the intensity measurements.

TABLE 1

Stoicheiometry of complexes in solution

Complex	Temperature (t/°C)	Ligand, L : Metal *
Co(γ-pic)$_4$T$_2$	−46	3·5
	−61	3·6
Co(γ-Etpy)$_4$T$_2$	−60	3·8
Co(γ-Etpy)$_2$T$_2$	−40	2·6
Co(β-Etpy)$_2$T$_2$	−61	2·5
Co(β-pic)$_2$T$_2$	−60	2·1

* Average values of at least four determinations. Values accurate to ± 0·5.

More detailed studies of the individual complexes with no added free ligand were performed first using both $CDCl_3$ and $(CD_3)_2CO$ as solvents in the temperature range ambient to *ca.* −90 °C.

The spectra of the individual complexes will now be described.

Co(γ-pic)$_4$T$_2$. (a) $CDCl_3$ *Solution* (*Figure* 1). The complex series of spectral changes are shown in the Figure. Basically, the changes involve a single set of three bands at ambient temperature changing into two sets of three bands of unequal intensities at −60 °C. At intermediate temperatures, two additional sets of surprisingly sharp bands were observed. We are confident that the two sets of bands at −60 °C are to be attributed to the *cis*- and *trans*-isomers of the L_4 complex with the *trans*-isomer predominating. At ambient temperature, the exchange rates between all complex species in solution were fast on the n.m.r. time scale so that a single set of fairly sharp bands was observed. On cooling to *ca.* 0 °C two 'intermediate' species were revealed whilst a rapid interconversion of *cis*- and *trans*-isomers continued. Further cooling resulted in the *cis–trans* exchange rate becoming slower with a consequent line broadening until by *ca.* −40 °C the rate became sufficiently slow for the individual isomer signals to be detected. On simple steric grounds the *trans*-isomer is likely to be dominant. The γ-CH_3 band of the minor isomer is almost coincident with the γ-CH_3 signal of one of the intermediates at temperatures where both species exist in detectable amounts. The 'intermediate' species must exchange much more slowly with the main isomers than do the latter between themselves since the bands of the intermediates are always sharp and are observed at higher temperatures than those due to the individual *cis*- and *trans*-isomers. It is postulated, for

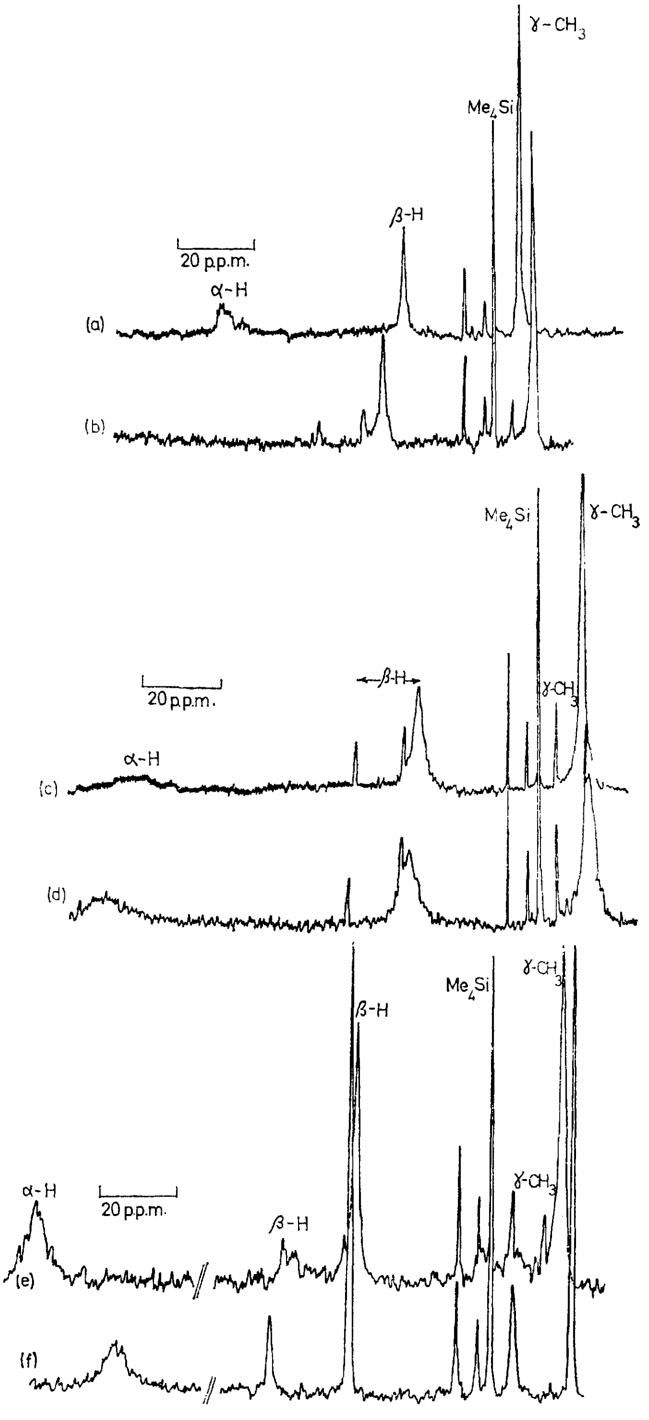
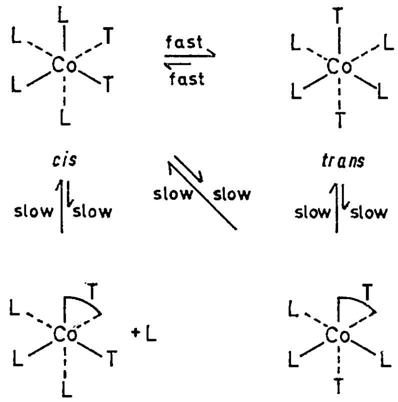


FIGURE 1 N.m.r. spectra of Co(γ-pic)$_4$T$_2$ in $CDCl_3$ at (a) 38, (b) 0, (c) − 10, (d) − 20, (e) − 40, and (f) − 60 °C

reasons given below, that these intermediates may be L_3 species, their abundance apparently decreasing as the temperature is lowered so that below −40 °C (in this case) they are undetectable. This would explain why no free diamagnetic ligand signals were observed at any temperature. Whilst free ligand is expected to be present in detectable amounts between *ca.* 0 °C and *ca.* −30 °C it will be in rapid exchange with co-ordinated ligands and at *ca.* −50 °C and below, where the exchange rate will be slow, the free ligand bands will have become too weak to be seen due to the low abundance of the L_3 species in this temperature range. The persistently sharp nature of the bands due to the intermediate L_3 species suggests that these species do not act as intermediates in the *cis–trans* isomeric exchange. It seems highly unlikely that a monomeric L_2 species or any type of polymeric species can account for the extra bands since these species are expected to become increasingly stable at lower temperatures in contrast to the observed trend. A scheme of exchange processes which would account for the n.m.r. observations is as follows:



N.B. Free γ-picoline may exhibit rapid exchange with all the above species above *ca.* −40 °C. The intermediates may alternatively be five-co-ordinate complexes involving only monodentate T groups.

It should be noted that only one set of bands per isomer is observed, even in the case of the *cis*-isomer where two sets are expected for the two chemically distinct γ-picoline environments. The implication is that at least at temperatures above −70 °C there is no distinction between these environments, presumably due to some rapid intramolecular exchange of ligands. A possible mechanism for such a process will be discussed later. The complex changes in the n.m.r. spectra with temperature were reflected in the temperature dependences of the various isotropic shifts. Figure 2 shows the trend of the β-H shifts, the discontinuities clearly indicating where additional species appear or disappear. Below *ca.* −50 °C the individual isomers obey the normal Curie Law behaviour and this was generally true for all the complexes.

(b) $(CD_3)_2CO$ *Solution.* The same general trends were observed but at somewhat lower temperatures than in $CDCl_3$. One difference, however, was that only one intermediate species was detected.

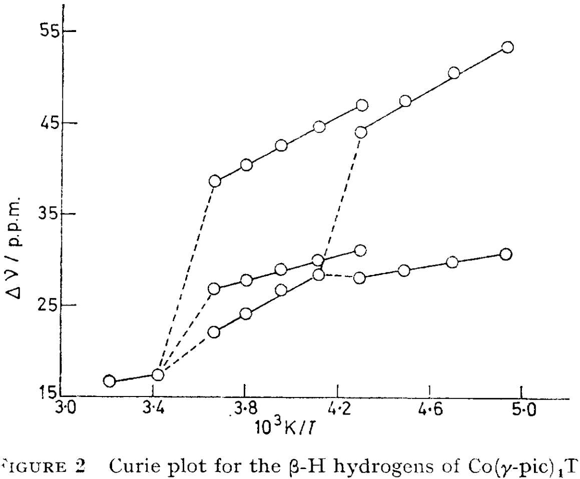
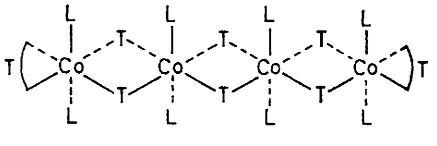


FIGURE 2 Curie plot for the β-H hydrogens of $Co(\gamma\text{-pic})_4T_2$ in $CDCl_3$

$Co(\gamma\text{-pic})_2T_2$.—(a) $CDCl_3$ *Solution.* The single set of broad bands, obtained at ambient temperature, split into two sets of similar relative intensity by *ca.* 0 °C and this feature was retained down to −60 °C. These changes may be straightforwardly interpreted as due to fast *cis–trans* isomer exchange at room temperature with this process becoming slow below 0 °C. The assignments of the bands (Table 2) are based on the spectrum of $Co(\gamma\text{-pic})_4T_2$ complex where the *trans*-isomer was considered to be dominant and gave rise to bands consistently upfield of the *cis*-isomer.

(b) $(CD_3)_2CO$ *Solution.* The spectra showed the same basic trend as for the $CDCl_3$ solution except that in addition to the *cis*- and *trans*-isomer bands a number of weak additional bands were detected. Of particular interest were the bands lying very close to the *trans*-isomer bands. These were thought to arise from a polymeric species formed exclusively from the *trans*-monomer. In view of the doublet appearance of the additional γ-CH_3 band it is tentatively suggested that these bands may be due to the tetrameric species:



Such a species would be expected to give rise to two slightly differing sets of shifts for the γ-picoline hydrogens.

$Co(\gamma\text{-Etpy})_4T_2$.—(a) $CDCl_3$ *Solution.* The spectral changes were generally analogous to those for $Co(\gamma\text{-pic})_4T_2$ except that a small amount of free ligand was detected in the low temperature region suggesting slight breakdown to an L_3 or L_2 complex. The former complex is more probable both on chemical shift grounds and on the fact that the intensities of the additional signals decreased with decreasing temperature.

(b) $(CD_3)_2CO$ *Solution.* At temperatures below

−60 °C, the spectra became very complex and have not been fully interpreted to date. Free ligand bands were not observed. In view of this fact and also since the spectra became increasingly complex on lowering the temperature, it is thought likely that the bands are due to numerous polymeric L_2 complexes.

TABLE 2

^{1}H N.m.r. shift data for the cobalt(II) complexes

Complex	Solvent	Temperature (t/°C)	α-H	Isotropic shifts ^{a}/p.p.m.			CH$_2$⁻	Unassigned	Species
				β-H	γ-H	CH$_3$⁻			
Co(γ-pic)$_4$T$_2$	CDCl$_3$	38	+62·0	+16·5		−8·9			
		−70	+124	+30·9		−25·2			*trans*
				+53·7		−7·9			*cis*
	(CD$_3$)$_2$CO	−90		+23·4		−35·0			*trans*
				+45·0		−23·4			*cis*
Co(γ-pic)$_2$T$_2$	CDCl$_3$	Ambient	+112	+27·3		−8·2			
		−60	+171 ^{b}	+29·2		−18·3			*trans*
			175 ^{b}	+46·4		−8·95			*cis*
	(CD$_3$)$_2$CO	−90		+38·2		−22·1			*trans*
				+59·0		−10·9			*cis*
				+37·0		−22·7, −23·1			Tetramer (?)
						−7·32, −18·4 −20·9			Polymer
Co(γ-Etpy)$_4$T$_2$	CDCl$_3$	38	+62·3	+16·3		−3·30	−8·20		
		−60	+120	+30·4		−9·18	−21·9		*trans*
			+149	+50·8		−5·61	−11·5		*cis*
	(CD$_3$)$_2$CO	−86	+118	+23·4		−14·3	−29·1		*trans*
			?	+42·0		−5·9	−14·6		*cis*
			+141 +160 +183	+29·5 +48·4 +54·9				−1·87 −10·7 −22·9 −30·7	Polymers
Co(γ-Etpy)$_2$T$_2$	CDCl$_3$	+38	+133	+27·1		−3·43	−7·60		
		−60	+180 ^{b}	+29·8		−2·40	−8·50		*trans*
			+184 ^{b}	+48·9		−11·2	−18·8		*cis*
	(CD$_3$)$_2$CO	−85	+201	+54·2		−3·54	−8·78		*cis*
			+184	+33·8, +34·6 +34·8, +35·7		−11·4 −11·7 −11·9 −12·2	−18·8, −19·4 −19·6, −20·2		*trans*-Polymer
				+62·9		−5·49	−14·2		?
				+42·6				−3·66	
				+47·3				+3·35	?
				+50·5				+3·90	
								+4·68	
Co(β-pic)$_2$T$_2$	CDCl$_3$	Ambient	c	c	c	c			
		−60	+150, +165	+30·3	−18·1	−3·66			*trans*
			+165, +199	+42·6	−2·43	+10·4			*cis*
	(CD$_3$)$_2$CO	−90		+52·2	−4·11	+16·0			*cis*
				+38·4 ^{d}	−23·5 ^{d}	−4·86 ^{d}			*trans*-Polymer
			Complex	+45·1, +50·3 +57·9, +67·2 +73·0		+4·75 +10·1		+4·42, +8·55 +10·0, +14·8 +16·5	Polymers ?
Co(β-Etpy)$_2$T$_2$	CDCl$_3$	+33	c	c	c	c	c		
		−60	+188 ^{b}, +220 ^{b}	+44·2	+9·66	+8·50	−2·38		*cis*
			+146,^{b} +164 ^{b}	+30·6	+7·74	−3·66	−2·38		*trans*
			?	+48·5	+0·26	+3·76	−15·5		?
	(CD$_3$)$_2$CO	−88			Highly complex				
Co(py)$_4$T$_2$	CDCl$_3$	−60	+132 +176 +183	+30·9 +45·0 +48·3	+8·9 −17·6				?

[a] Shifts are relative to the diamagnetic ligand values. [b] Assignments could possibly be reversed. [c] Broad, time-averaged bands. No chemical shifts given due to tetramethylsilane signal being obscured. [d] Values refer to the centres of the quartets.

Co(γ-Etpy)$_2$T$_2$.—(a) CDCl$_3$ *Solution* (*Figure* 3). These spectra could be straightforwardly interpreted as due to the presence of almost equal amounts of *cis*- and *trans*-isomers which at ambient temperatures undergo rapid interconversion but which below *ca.* 0 °C become slowly interconverting on the n.m.r. time scale. No bands due to intermediate species were detected.

(b) (CD$_3$)CO *Solution* (*Figure* 4). At −41 °C, the similarity of the spectrum to that in CDCl$_3$ solution suggests that the two main sets of bands are due to *cis*- and *trans*-species. The *trans*-isomer bands appear to be split into four closely separated lines of approximately equal intensity. This multiplet structure remains virtually unchanged on further cooling and suggests that it arises from a polymeric complex, based on the *trans*-monomer and necessarily involves a bridging trifluoroacetate group. The sets of four lines may be associated with the four slightly differing ligand environments of a linear octameric complex $[Co(\gamma\text{-}Etpy)T_2]_8$ but is more likely to be due to a mixture of polymeric structures of varying chain length. The postulated *cis*-monomer and *trans*-linear polymers are significant species over the range −40 °C to −80 °C, whilst at lower temperatures other species, presumably unknown polymeric forms of the *cis*-monomer, become more abundant.

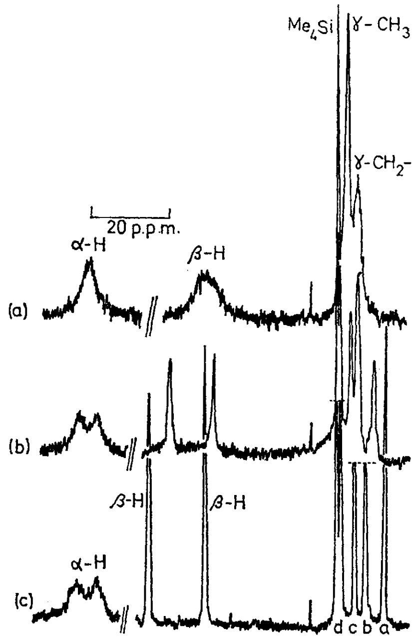


FIGURE 3 N.m.r. spectra of $Co(\gamma\text{-}Etpy)_2T_2$ in $CDCl_3$ at (a) + 38, (b) 0, and (c) − 30 °C (peaks a, c, assigned to $\gamma\text{-}CH_2\text{-}$ and peaks b and d to $\gamma\text{-}CH_3$)

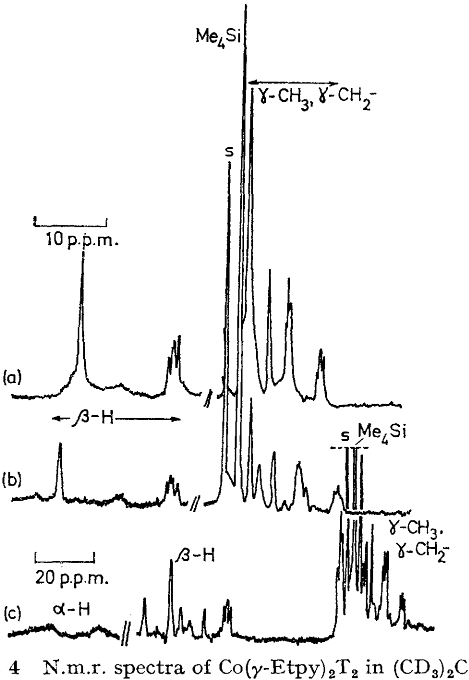


FIGURE 4 N.m.r. spectra of $Co(\gamma\text{-}Etpy)_2T_2$ in $(CD_3)_2CO$ at (a) − 41, (b) − 64, and (c) − 85 °C (s denotes solvent peak)

$Co(\beta\text{-}pic)_2T_2$.—(a) $CDCl_3$ *Solution.* This complex exhibited the same trend as the other L_2 complexes discussed so far.

(b) $(CD_3)CO$ *Solution.* Very complex spectra were obtained below −50 °C which have not yet been fully interpreted. However, an interpretation analogous to that for $Co(\gamma\text{-}Etpy)_2T_2$ seems likely.

$Co(\beta\text{-}Etpy)_2T_2$.—(a) $CDCl_3$ *Solution.* At room temperature a single set of broad bands was observed indicating an intermediate rate of *cis–trans* isomeric exchange. At lower temperatures bands characteristic of individual *cis*- and *trans*-isomers were observed together with a very weak third set of bands. The latter is attributed to a trace of polymeric material.

(b) $(CD_3)_2CO$ *Solution.* The tendency towards polymerisation in solution is particularly reflected in the complex spectra in this solvent. At −88 °C, the complexity is such that in the β-H region alone ten distinct bands were observed. The characteristic four-line multiplet as observed for $Co(\gamma\text{-}Etpy)_2T_2$ is again in evidence, suggesting as before a polymer based on the *trans*-monomer.

$Co(py)_4T_2$ *and* $Co(py)_2T_2$.—$CDCl_3$ *Solution.* These complexes were virtually insoluble in all common organic solvents. All attempts to obtain informative ambient temperature spectra failed. However, at −60 °C in $CDCl_3$, some weak bands were detected. For both the L_4 and L_2 complexes, however, the chemical shifts were within experimental error identical (Table 2). It seems very probable that both complexes undergo decomposition on dissolution in $CDCl_3$ with subsequent reassociation with pyridine to give similar equilibrium mixtures of species.

^{19}F *N.M.R. Spectra.*—The results of these studies are summarised in Table 3. In general, they completely bear out the observations and conclusions drawn from the ^1H spectra. At ambient temperatures, two bands were observed indicative of the trifluoroacetate groups in the *cis*- and *trans*-isomers. The relative intensities

TABLE 3

^{19}F N.m.r. shift data

Complex [b]	Temperature (t/°C)	Shifts/p.p.m. [a]		Relative intensities
$Co(\gamma\text{-}pic)_4T_2$	70	+89		
	33·5	+102	+139	12 : 1
$Co(\gamma\text{-}pic)_2T_2$	33·5	+90	+141	1 : 1
$Co(\gamma\text{-}Etpy)_4T_2$	33·5	+89, +102, +142		0·5 : 10 : 1
$Co(\gamma\text{-}Etpy)_2T_2$	60	+100		
	33·5	+88	+138	1 : 1
	−45	+121	+199	
$Co(\beta\text{-}pic)_2T_2$	60	+101		
	33·5	+90	+142	1 : 1
	−30	+118	+188	
$Co(\beta\text{-}Etpy)_2T_2$	60	*c*		
	33·5	+90	+144	1 : 1
	−30	+118	+190	

[a] Shifts relative to external CF_3CO_2H ($\delta = 0$). Positive δ denotes low field shift. Values accurate to ±1 p.p.m. [b] Complexes in $CDCl_3$ (concn. *ca.* 0·2 mol dm^{-3}). [c] Very broad absorption band just detectable. Great width indicative of coalescence of low temperature bands.

of these bands support the observations of the ^1H spectra, namely that in the L_4 complexes the *trans* : *cis* abundance ratio is *ca.* 10 : 1 and in the L_2 complexes is *ca.* 1 : 1. The weak third band observed for $Co(\gamma\text{-Etpy})_4T_2$ may be associated with the L_3 complex postulated from the ^1H spectra. The bands were somewhat concentration dependent as is usual for ^{19}F shifts but the solvent shifts were minor compared to the absolute magnitudes of the shifts. On raising the temperature of the samples above room temperature the bands invariably broadened to such an extent that they became undetectable and then reappeared as single time-averaged bands. The coalescence temperatures were in the range 40—60 °C, appreciably higher than in the ^1H spectra on account of the much larger internal chemical shifts between exchanging signals in the ^{19}F spectra.

CONCLUSIONS

The general trend in the observed ^1H shifts, namely that α-H $\gg$ β-H > γ-H, supports the well established contention that contact shifts in pyridine-type ligand complexes are dominated by σ delocalisation. However, on account of the magnetic anisotropy of octahedral Co^{II}, we must expect sizeable dipolar contributions to the isotropic shifts in the present complexes. Separation of the observed shifts into contact and dipolar contributions will be discussed in a later paper [12] which will also include a theoretical treatment of the shifts of both the Co^{II} and corresponding Ni^{II} complexes. In the case of the substituent $-CH_2-$ and $-CH_3$ shifts, these are invariably to high field for γ-substituents and, for γ-ethyl substituents, such that $-CH_2- > -CH_3$. For β-substituents, the shifts are to low field of the diamagnetic positions and such that $-CH_3 > -CH_2-$.

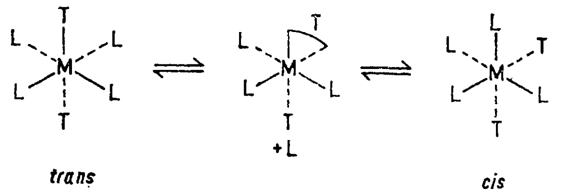
The question concerning the theoretical interpretation of the ^1H isotropic shifts of pyridine-type ligands, about which there has been considerable recent controversy,[13-16] will be discussed in more detail in a later paper.[12] For Co^{II} in contrast to Ni^{II} complexes there is also the problem of the dipolar contribution to the observed shifts. However, given certain important criteria, separation of the contact and dipolar contributions can be achieved [6,17] in cases where shift data are available for corresponding Ni^{II} complexes.

The importance of the dipolar contribution to the observed shifts in the Co^{II} complexes may be qualitatively assessed in the extents to which the shifts for corresponding hydrogens in *cis*- and *trans*-complexes differ. In the case of the large α-H shifts, these are dominated by the σ-contact mechanism. The dipolar contribution is almost negligible and distinction between isomers is often small. For example, in $Co(\gamma\text{-Etpy})_2T_2$, at -60 °C, $|\delta(\alpha\text{-H},cis) - \delta(\alpha\text{-H},trans)| = 4$ p.p.m. For β-H shifts, the dipolar contribution is of comparable importance to the contact contribution; *e.g.* for $Co(\gamma\text{-Etpy})_2T_2$, $|\delta(\beta\text{-H},cis) - \delta(\beta\text{-H},trans)| = 19.1$ p.p.m. For substituents, the dipolar contribution rivals the π-spin polarisation in importance and there is again a clear distinction between *cis*- and *trans*-isomers. When the corresponding Ni^{II} complexes are discussed [12] it will be strikingly evident that the chemical shift distinction between *cis*- and *trans*-isomers is very small, due to the fact that no dipolar shifts can arise from regular octahedral Ni^{II} complexes in their $^3A_{2g}$ ground state.

From these n.m.r. studies it is evident that the complexes in solution are kinetically labile and often somewhat thermodynamically unstable leading to breakdown and/or polymerisation of the original complex. The present studies have illustrated the operation of the following three types of exchange process.

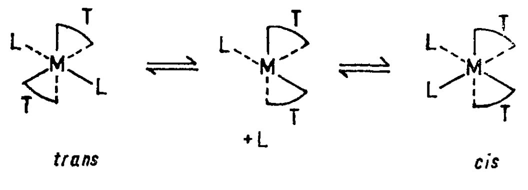
(1) *Intermolecular exchange involving free and co-ordinated ligand molecules.* In solvents containing free ligand, rapid exchange occurs at ambient temperatures. Below *ca.* -30 °C, the exchange becomes slow on the n.m.r. time scale and bands due to the co-ordinated and free ligand molecules may be 'frozen out.'

(2) cis–trans *Isomerism.* This process becomes slow on the ^1H n.m.r. time scale by *ca.* 0 °C for L_2 complexes and by *ca.* -50 °C for L_4 complexes. A number of mechanisms have been suggested for *cis–trans* isomerism of octahedral complexes of the types ML_4X_2 and ML_2X_2. A possible mechanism for the present L_4 complexes would be



where the postulated L_3 intermediate may be a six-co-ordinate complex (as shown above) or a five-co-ordinate trigonal bipyramidal or tetragonal pyramidal structure, involving only monodentate T ligands. It should be noted that this postulated intermediate must possess a different structure and stability to the L_3 intermediates which have been postulated to explain the additional bands in the ^1H spectra at intermediate temperatures. These latter species play no part in the *cis–trans*-isomer interconversion since their n.m.r. signals remain very sharp at all temperatures.

A possible mechanism for the *cis–trans* interconversion of the L_2 complexes is:



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[12] Part IV, P. Anstey and K. G. Orrell, *J.C.S. Dalton*, accepted for publication.

[13] W. De W. Horrocks and D. L. Johnston, *Inorg. Chem.*, 1971, **10**, 1835.

[14] R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, 1972, **11**, 668.

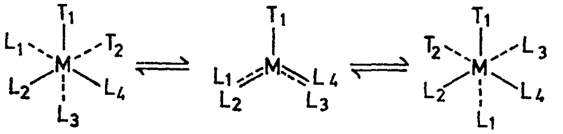
[15] R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, 1970, **92**, 66.

[16] W. De W. Horrocks, *Inorg. Chem.*, 1973, **12**, 1211.

[17] W. De W. Horrocks, *Inorg. Chem.*, 1970, **9**, 690.

In this case we postulate a trigonal bipyramidal L_1 intermediate.

(3) *Intramolecular ligand scrambling.* This motional process is postulated to account for the single set of ligand hydrogen signals observed for the *cis*-L_4 complexes. The rate process must always be fast on the n.m.r. time scale and is almost certainly intramolecular since any intermolecular process would almost inevitably lead to *cis–trans* interconversion. Stereochemical non-rigidity in molecules due to ligand scrambling processes is now recognised as an important phenomenon in inorganic chemistry.[18] Many of the suggested mechanisms for scrambling processes in octahedral complexes involve isomerisation but a trigonal twist mechanism first proposed by Bailar[19] to account for racemisation without isomerisation of tris chelate complexes represents one possible mechanism for the scrambling process in the present complexes.



The process involves a trigonal twist which causes the L_1 and L_4 ligands to take up the original sites of L_3 and L_2, respectively, and *vice versa.* It should be noted that other twisting mechanisms are possible[20] which could account for the present n.m.r. results. However, until the scrambling process can be slowed down to enable n.m.r. line shape studies to be carried out it is not possible to give preference to one particular twisting mechanism. If this scrambling phenomenon is occurring in the *cis*-L_4 complexes, it will almost certainly be present in the other L_4 and L_2 isomers. However, its detection in these isomers will not be possible by n.m.r. as the process involves exchange between identical ligand environments. Nevertheless, it is hoped to carry out further work into the generality and mechanism of this scrambling process using a wider range of complexes.

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[3/1995 *Received, 28th September,* 1973]

[18] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, 1972.

[19] J. C. Bailar, *J. Inorg. Nuclear Chem.*, 1958, **8**, 165.

[20] C. S. Springer and R. E. Sievers, *Inorg. Chem.*, 1967, **6**, 852.