Trifluoroacetate Complexes of Cobalt(II), Nickel(II), and Copper(II) with Pyridine-type Ligands. Part 5.[1-4] Dynamic Nuclear Magnetic Resonance Studies of *cis–trans* Isomerism

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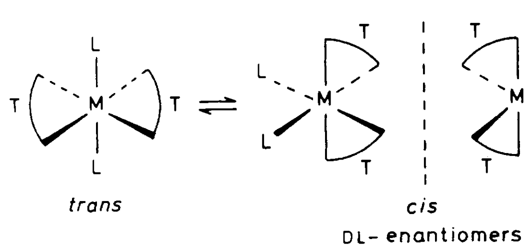
Dynamic ^1H n.m.r. studies of complexes of general type $[ML_2(O_2CR)_2]$ [M = Co^{II} or Ni^{II}; L = 3Me-py, 4Me-py, or 4Et-py (py = pyridine); R = CF_3, CF_2H, CFH_2, C_2F_5, or C_3F_7] have yielded accurate energies for the *cis–trans* interconversion of these complexes. For cobalt(II) complexes $\Delta G^‡$ values lie in the range 47—60 kJ mol^{-1}, whereas for nickel(II) complexes values are substantially higher being 67—71 kJ mol^{-1} for trifluoroacetate complexes. Data for $\Delta S^‡$ imply that the mechanisms of the isomerisation are dependent on the carboxylate ligand O_2CR and become more dissociative in nature in the order R = $CF_3 < CF_2H < CFH_2 < C_2F_5 < C_3F_7$, this order also applying to the relative magnitudes of $\Delta H^‡$ values. Isomerism in the related $[ML_4(O_2CR)_2]$ complexes, where the O_2CR ligands are unidentate, is shown to be a much more facile, dissociative process, detectable amounts of two additional species thought to be *cis*- and *trans*-$[ML_2(O_2CR)_2]$ also being present.

Previous parts [1-4] of this work have described the preparations, thermal decompositions, and spectroscopic [electronic, vibrational, and (primarily) n.m.r.] studies of metal trifluoroacetates complexed with pyridine-type ligands. Variable temperature n.m.r. studies [2] have established the presence of *cis–trans* equilibria in the Co^{II} and Ni^{II} complexes $[ML_4T_2]$ and $[ML_2T_2]$ [L = py, Me-py, or Et-py (py = pyridine); T = O_2CCF_3] where T is acting as a unidentate and bidentate ligand respectively. In order accurately to measure the energies of *cis–trans* interconversion in these complexes we have carried out total n.m.r. bandshape analyses on portions of the ligand proton spectra of the complexes $[ML_2(O_2CR)_2]$ (M = Co^{II} or Ni^{II}; L = 3Me-py, 4Me-py, or 4Et-py; R = CF_3, CF_2H, CFH_2, C_2F_5, or C_3F_7). We now report our findings and show how the energies of the isomerisation process depend on the transition metal M, the carboxylate ligand O_2CR, and the pyridine-type ligand L. Mechanistic implications of the thermodynamic data are also discussed. A brief comparison is also made with the complexes of stoicheiometry $[ML_4T_2]$, but energy calculations based on full-bandshape fittings were not feasible here due to the presence of additional complex species.

cis–trans Isomerism of the type shown below has been previously detected by observing the changes of the ligand ^1H and trifluoroacetate ^{19}F signals with temperature. Signals due to individual isomers are observed at low temperatures for the ligand protons of cobalt(II) complexes and at ambient temperatures for nickel(II) complexes. At higher temperatures these signals coalesce and eventually produce sharp averaged signals due to the rapid *cis–trans* interconversion. These relatively slow isomer exchange rates are thought to be primarily associated with the co-ordinating properties of the perfluoro-acid ligands as no similar isomerisms have been observed in other complexes of stoicheiometry $[ML_2X_2]$ [5,6] where L is a pyridine-type ligand and X is other than O_2CCF_3. However, there is some evidence for the existence of scrambling of acetate-type ligands in the complexes $[Ni(edta)]^{2-}$ (edta = ethylenediaminetetra-acetate) [7] and $[Ni(nta)_2]^{4-}$ (nta = nitrilotriacetate),[8] and the exchange kinetics of inner- and outer-sphere trifluoroacetate complexes of nickel(II) have recently been studied.[9] In the present complexes, however, all the evidence suggests that the pyridine-type ligands rather than the perfluoro-acid ligands are the labile groups in the *cis–trans* interconversion. In view of the novelty of this process we therefore wished to measure accurately the activation energies involved and to examine the effects of varying M, L, and O_2CR. Accurate n.m.r. bandshape fittings of the ^1H spectra were therefore performed as described later.



It was hoped to investigate the effect of changing the metal by studying the iron(II) and zinc(II) complexes in addition to those of cobalt(II) and nickel(II). The complex $[Fe(4Me\text{-}py)_2(O_2CCF_3)_2]$ was prepared as a green solid following the method of Baillie *et al.*[10] but its high sensitivity to aerial oxidation, particularly in solution, made it unsuitable for any extended variable temperature n.m.r. studies. Some evidence for *cis–trans* interconversion was, however, obtained. The zinc complex $[Zn(4Me\text{-}py)_2(O_2CCF_3)_2]$ was perfectly stable but the ^1H and ^{19}F shifts typical of a diamagnetic species showed very little temperature dependence of lineshape and therefore precluded any study of *cis–trans* equilibrium. Our bandshape fittings are thus based on cobalt(II) and nickel(II) complexes of stoicheiometry $[ML_2(O_2CR)_2]$. The decision to study the L_2 rather than the L_4 complexes was influenced by practical considerations. For instance, additional signals are invariably observed in the low-temperature solution spectra of the L_4 complexes, thus complicating the bandshape fittings. Furthermore, the isomeric abundances, whilst usually approximately equal for the L_2 complexes, are very different (*e.g.* 1 : 5) in many L_4 complexes. Both factors therefore make the L_2 complexes more amenable to accurate band-fitting methods.

Experimental

Materials.—The complexes $[ML_2(O_2CCF_3)_2]$ (M = Co^{II} or Ni^{II}; L = alkylpyridine) were prepared as previously described by Orrell and co-workers [2] following the general method of Lever and Ogden.[11] The complexes $[Co(4Me\text{-}py)_2(O_2CC_2F_5)_2]$ and $[Co(4Me\text{-}py)_2(O_2CC_3F_7)_2]$ reported

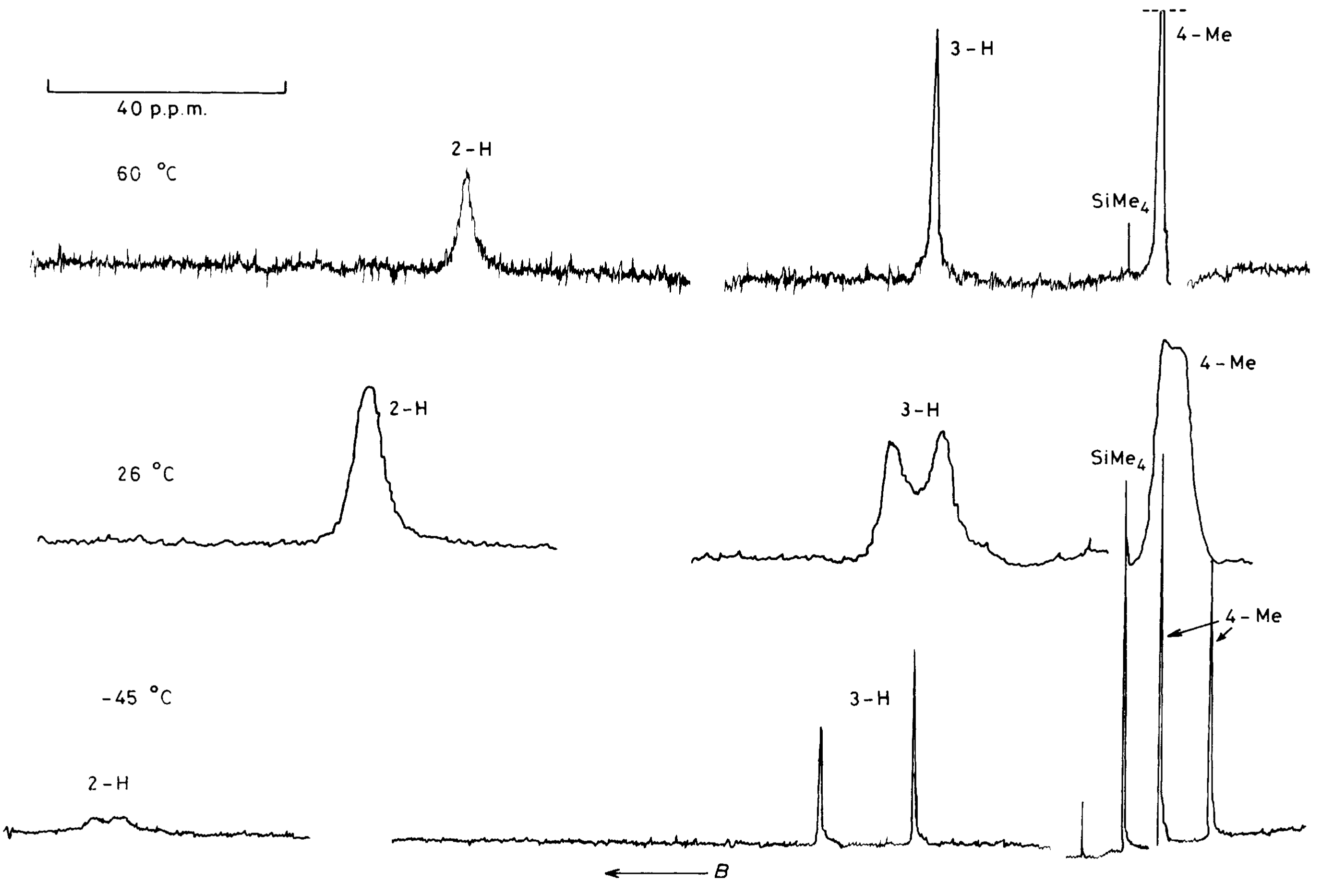


Figure 1. Variable temperature 100-MHz ^1H n.m.r. spectra of $[Co(4Me\text{-}py)_2(O_2CCF_3)_2]$ showing the effects of varying rates of *cis–trans* interconversion

previously[12] and the new complexes $[M(4Me\text{-}py)_2(O_2CR)_2]$ ($R = CF_2H$ or CFH_2) were prepared by analogous routes. Satisfactory C, H, N, and F microanalyses were achieved provided that additional oxidant was used in the combustion analysis.

Spectra.—Proton n.m.r. spectra were recorded on a JEOL MH-100 spectrometer operating at 100 MHz in continuous wave mode. The complexes were dissolved in $CDCl_3$ and recorded at temperatures in the range 60 to −60 °C. Temperatures were controlled with a standard JES-VT-3 unit and usually measured with a copper–constantan thermocouple immersed directly in the n.m.r. sample. Samples were not spun during spectral measurement using this arrangement. In any case, tests showed that spinning would not have significantly improved the spectral quality on account of the relatively large ($\Delta\nu_{\frac{1}{2}} > 30$ Hz) natural linewidths of the paramagnetic signals. Temperature measurements were taken at the beginning, midway, and at the end of the spectral recordings. Spectra were acceptable if the temperature drift did not exceed 0.5 °C, which was usually the case. In order to measure the fast-exchange spectra of the nickel(II) complexes and the complex $[Co(4Me\text{-}py)_2(O_2CC_3F_7)_2]$ it was necessary to seal the n.m.r. sample tubes, in which cases probe temperatures were measured immediately before and after recording the spectra using either a thermocouple or an accurate mercury thermometer.

In order to accommodate the large chemical shifts arising from these paramagnetic complexes an accurately calibrated wide-sweep attachment NM-WS-1 was used.

Bandshape Analyses.—Total bandshape analyses of exchange-broadened n.m.r. signals have most commonly been based on visual matchings of computer synthesised spectra (obtained from a set of 'static' parameters) with experimental spectra measured for a series of temperatures. Whilst this method works well for many systems it is preferable to eliminate the subjective element of visual fitting by using a program that will internally calculate the optimum fit by an iterative procedure. The recent DNMR-5 program of Stephenson and Binsch[13] incorporates this method. The ^1H spectra of $[ML_2(O_2CR)_2]$ ($M = Co^{II}$ or Ni^{II}) were highly suited to this rigorous iterative approach and this procedure was therefore adopted in the following way. An A/D converter was used as an interface between the n.m.r. spectrometer and a Digiac (Digico Ltd.) computer in a similar manner to that used by Cox *et al.*[14] A full sweep of the chart recorder was digitised by 3001 data points but in practice it was found that 601 were sufficient reliably to represent the chosen portions of experimental spectra. It was found beneficial in many instances to smooth numerically the digitised spectra using a published least-squares method.[15] This technique was particularly effective in the very broad spectra ($\Delta\nu_{\frac{1}{2}} \sim 700$ Hz) often observed for cobalt(II) complexes around the coalescence temperature. Linear changes in base line levels were also allowed for in the digitisation. Both the observed and calculated spectra were normalised and matched by ensuring that the maximum intensity data points coincided. A non-linear least-squares analysis of calculated and observed spectra was then performed using the full bandshape equation as expressed by Nakagawa.[16] Convergence of the iterative

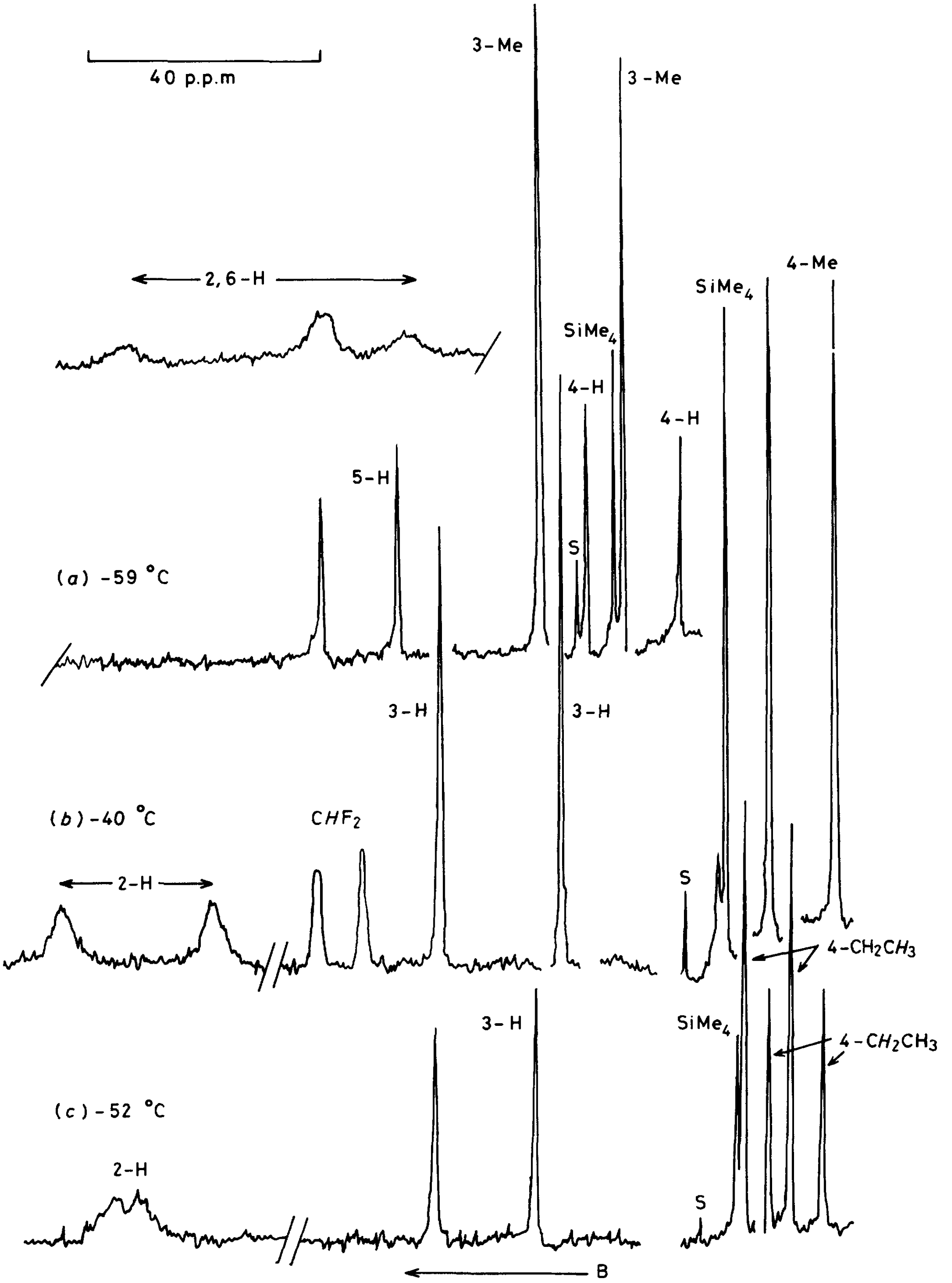


Figure 2. Low temperature 100-MHz ^{1}H n.m.r. spectra of (*a*) [Co(3Me-py)$_2$(O$_2$CCF$_3$)$_2$], (*b*) [Co(4Me-py)$_2$(O$_2$CCF$_2$H)$_2$], and (*c*) [Co(4Et-py)$_2$(O$_2$CCF$_3$)$_2$] showing the distinct *cis* and *trans* isomers. S = solvent

procedure was accepted if the calculated incremental change ($\Delta\tau_A$) in the parameter τ_A (the lifetime of site A) was <0.5% of the previously calculated τ_A value. Non-convergence was occasionally a problem when the initial value of τ_A was too distant from the proper value. A 'damping' procedure[17] was tested in an attempt to overcome this difficulty but this produced a considerable slowing down of the convergence and was not normally used.

Results

The spectra of [Co(4Me-py)$_2$(O$_2$CCF$_3$)$_2$] shown in Figure 1 are typical of the changes arising from the varying rate of *cis–trans* interconversion. Clear isomeric distinction is apparent in the low temperature spectra of this complex and of other Co^{II} complexes (Figure 2). The low temperature spectra of [Co(4Me-py)$_2$(O$_2$CCFH$_2$)$_2$] were notable in that

Table 1. 100-MHz ^{1}H static parameters used in band shape fittings

Complex	Signal fitted	p_A	Natural linewidths/Hz $\Delta\nu_{\frac{1}{2}}(A)$	Natural linewidths/Hz $\Delta\nu_{\frac{1}{2}}(X)$	$(\nu_A - \nu_X)$ [a]/Hz x	$(\nu_A - \nu_X)$ [a]/Hz y
$[Co(4Me\text{-}py)_2(O_2CCFH_2)_2]$	4-Me	0.58	107—200 [b]	95.0	−610	550
$[Co(4Me\text{-}py)_2(O_2CCF_2H)_2]$	4-Me	0.50	45.0	69.0	−818	433
$[Co(4Me\text{-}py)_2(O_2CCF_3)_2]$	3,5-H	0.50	57.7	39.3	−1 126	613
$[Co(4Me\text{-}py)_2(O_2CC_2F_5)_2]$	3,5-H	0.50	43.3	37.0	*c*	*c*
$[Co(4Me\text{-}py)_2(O_2CC_3F_7)_2]$	3,5-H	0.50	57.2	49.0	−985	526
$[Co(3Me\text{-}py)_2(O_2CCF_3)_2]$	5-H	0.50	61.2	44.7	−760	437
$[Co(4Et\text{-}py)_2(O_2CCF_3)_2]$	3,5-H	0.50	52.7	32.2	−1 351	678
$[Ni(4Me\text{-}py)_2(O_2CCF_3)_2]$	4-Me	0.50	42—59 [d]	42—59 [d]	80.0	0.0
$[Ni(3Me\text{-}py)_2(O_2CCF_3)_2]$	3-Me	0.67	56.8	94.6	79.6	39.7
$[Ni(4Et\text{-}py)_2(O_2CCF_3)_2]$	4-CH_2CH_3	0.70	98.0	90.0	202	0.0
$[Co(4Me\text{-}py)_4(O_2CCF_3)_2]$	4-Me	0.72	*e*	*e*	−734	445

[a] Temperature dependence of chemical shift difference given by $(\nu_A - \nu_X) = x + y(10^3\text{K}/T)$. [b] Temperature-dependent linewidth given by $\Delta\nu_{\frac{1}{2}}(A) = 590 - 116.2(10^3\text{K}/T)$. [c] Non-linear temperature dependence (see text). [d] Temperature-dependent linewidth given by $\Delta\nu_{\frac{1}{2}}(A) = \Delta\nu_{\frac{1}{2}}(X) = 147 - 32(10^3\text{K}/T)$. [e] Not measured.

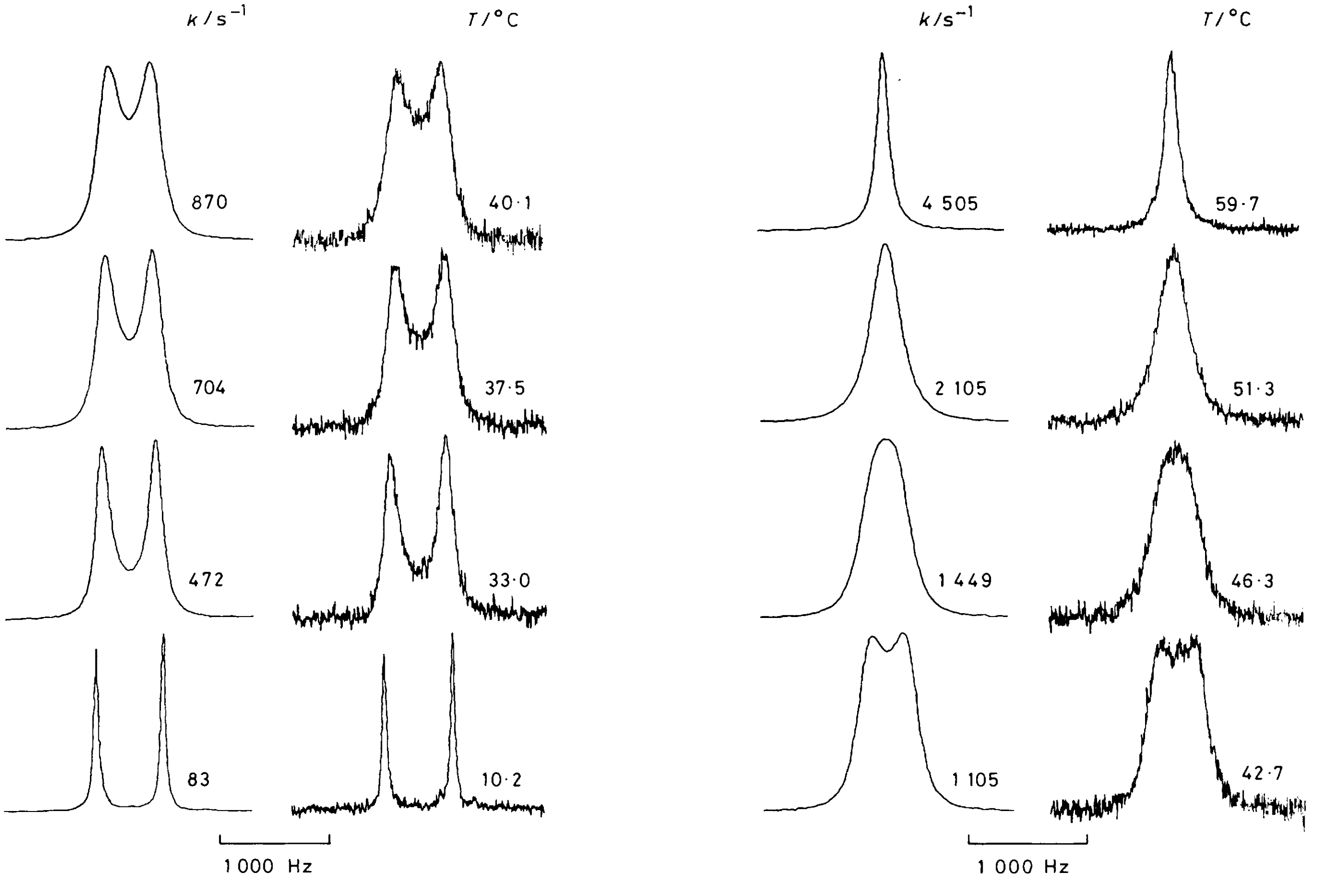


Figure 3. Comparison of the experimental and computer synthesised spectra of $[Co(4Me\text{-}py)_2(O_2CC_2F_5)_2]$ showing the ' best-fit ' rate constants for each temperature

four signals of similar intensity were observed for the CFH_2 protons rather than the expected two signals. The signal separations (~10 p.p.m.) were far too large to be due to indirect $^1J_{FH}$ couplings and imply a chemical shift non-equivalence of the geminal protons of both the *cis* and *trans* isomers. The explanation of this observation is obscure but a somewhat analogous effect was observed in the $-CF_2-$ signals of $[Co(4Me\text{-}py)_2(O_2CC_2F_5)_2]$.[12]

For each complex the most appropriate signals for the band-shape fittings were chosen. These were usually the 3-H and/or 5-H protons or the protons of the alkyl substituent (Table 1). The isomerisations were represented by simple two-site exchanges, $A \rightleftharpoons X$, characterised by the isomer populations p_A and p_X, the chemical shift difference, $|\nu_A - \nu_X|$, and the natural bandwidths at half maximum height $\Delta\nu_{\frac{1}{2}}(A)$ and $\Delta\nu_{\frac{1}{2}}(X)$. The populations were determined by standard integration methods, no appreciable temperature dependencies being noted in most cases.

Table 2. Arrhenius and Eyring parameters for *cis–trans* interconversion in octahedral Co^{II} and Ni^{II} complexes

Complex	Fitting method [a]	Points [b]	ΔT [c]/K	T_c [d]/K	E_a/kJ mol^{-1}	$\log_{10}A$	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta G^\ddagger$ [e]/ kJ mol^{-1}
$[Co(4Me\text{-}py)_2(O_2CCFH_2)_2]$	V	8	56	263	52.2 ± 1.4	13.6 ± 0.3	50.0 ± 1.4	+9 ± 6	47.4 ± 0.3
$[Co(4Me\text{-}py)_2(O_2CCF_2H)_2]$	LS	9	61	282	46.5 ± 1.0	11.7 ± 0.2	44.3 ± 1.0	−28 ± 4	52.7 ± 0.2
$[Co(4Me\text{-}py)_2(O_2CCF_3)_2]$	LS	11	89	301	45.2 ± 1.9	11.0 ± 0.3	42.8 ± 1.9	−42 ± 7	55.4 ± 0.3
$[Co(4Me\text{-}py)_2(O_2CC_2F_5)_2]$	LS	9	50	317	64.3 ± 1.2	13.7 ± 0.2	61.8 ± 1.1	+8 ± 4	59.3 ± 0.2
$[Co(4Me\text{-}py)_2(O_2CC_3F_7)_2]$	LS	9	67	322	70.3 ± 1.4	14.6 ± 0.2	67.8 ± 1.4	+26 ± 5	60.0 ± 0.2
$[Co(3Me\text{-}py)_2(O_2CCF_3)_2]$	LS	10	71	301	55.0 ± 0.8	12.7 ± 0.1	52.6 ± 0.8	−10 ± 3	55.6 ± 0.1
$[Co(4Et\text{-}py)_2(O_2CCF_3)_2]$	LS	8	60	300	47.6 ± 1.3	11.5 ± 0.2	45.2 ± 1.3	−33 ± 5	55.0 ± 0.2
$[Ni(4Me\text{-}py)_2(O_2CCF_3)_2]$	LS	7	57	330	55.5 ± 2.9	10.7 ± 0.5	52.8 ± 2.9	−49 ± 9	67.5 ± 0.5
$[Ni(3Me\text{-}py)_2(O_2CCF_3)_2]$	V	6	40	341	76.5 ± 3.2	13.8 ± 0.5	73.6 ± 3.2	+10 ± 9	70.5 ± 0.4
$[Ni(4Et\text{-}py)_2(O_2CCF_3)_2]$	V	7	48	348	70.2 ± 4.1	12.7 ± 0.6	67.3 ± 4.1	−11 ± 12	70.6 ± 0.8
$[Co(4Me\text{-}py)_4(O_2CCF_3)_2]$	C	—	—	243	—	—	—	—	45 [d]

[a] Visual (V) or iterative least-squares (LS) fitting methods; C = closed form approximation (see text). [b] Number of points used for the Arrhenius and Eyring plots. [c] Temperature variation covered in lineshape fittings. [d] Coalescence temperature. [e] Calculated at T = 298.15 K except where otherwise stated.

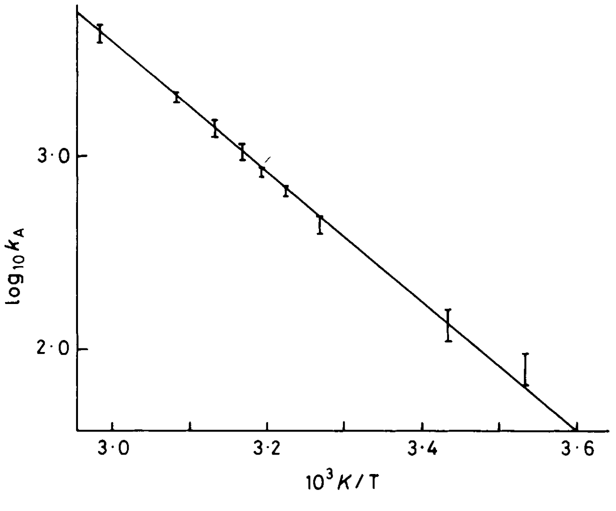


Figure 4. Arrhenius plot for $[Co(4Me\text{-}py)_2(O_2CC_2F_5)_2]$

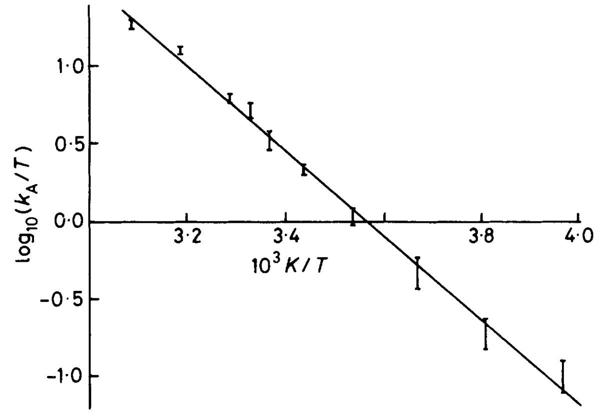


Figure 5. Eyring plot for $[Co(3Me\text{-}py)_2(O_2CCF_3)_2]$

The appreciable temperature dependencies of the isotropic shifts were accurately measured from the slow exchange spectra. In all complexes with one exception the shift differences $|\nu_A - \nu_X|$ followed a T^{-1} dependence as expected for Curie-law dependent isotropic shifts. This enabled shift differences in the intermediate and fast-exchange regions to be found by extrapolation. For $[Co(4Me\text{-}py)_2(O_2CC_2F_5)_2]$ the shift data could not be accommodated using a T^{-1} relationship and a non-linear extrapolation was necessary. Non-Curie-law behaviour is not unusual and is in fact predicted [18] for octahedral cobalt(II) complexes with appreciable Zeeman mixing of the excited electronic states with the ground state. However, the reason why this particular complex alone showed such behaviour is not immediately apparent.

The half-height linewidths in the absence of exchange, $\Delta\nu_{\frac{1}{2}}$, could usually be obtained from the trends in the low temperature spectra. The values chosen (Table 1) were, in most cases, either the minimum values measured before solvent viscosity effects became apparent or the averages of several low temperature values. The choice of the correct values was more difficult for the nickel(II) complexes where neither the slow- nor fast-exchange extremes could be properly reached experimentally using $CDCl_3$ as solvent. Approximate values were therefore estimated from the observed trends in the low temperature spectra.

The rate constants, k_A (= τ_A^{-1}), for exchange from site A to site X were extracted by iterative least-squares fittings of the calculated and observed spectra as described earlier. The fittings of the 3,5-hydrogen region of $[Co(4Me\text{-}py)_2(O_2CC_2F_5)_2]$ are illustrated in Figure 3. The rate constants and subsequent Arrhenius and Eyring energy parameters (Table 2) are based on the conversion: more abundant ⟶ less abundant isomer. Arrhenius and Eyring plots are shown in Figures 4 and 5, the straight lines being based on a weighted linear regression analysis,[19] data points around the coalescence temperature being weighted most heavily. In Figures 4 and 5, the reciprocal lengths of the error bars represent the relative weightings of each point. Errors in temperature measurements were considered to be negligible compared to errors in the rate constants. The errors in the energy parameters are standard deviations, σ, calculated from the regression analysis, those for $\Delta G^\ddagger$ being calculated from equation (1), where

$$\sigma^2(\Delta G^\ddagger) = \sigma^2(\Delta H^\ddagger) - T^2\sigma^2(\Delta S^\ddagger) - 2T\rho\sigma(\Delta H^\ddagger)\sigma(\Delta S^\ddagger) \quad (1)$$

the correlation coefficient ρ is >0.99, following the procedure of Binsch and Kessler.[20] This expression realistically reflects the relative insensitivity of $\Delta G^\ddagger$ values to errors in either the rate constant k_A or temperature measurement.

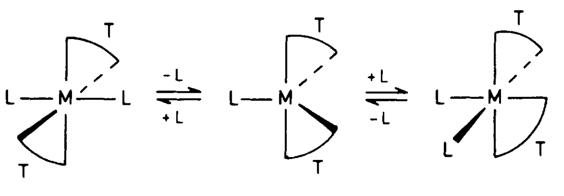
The energy data reported in Table 2 therefore represent the most accurate data that could be achieved for simple $A \rightleftharpoons X$ exchange systems. The employment of iterative total bandshape analysis, accurate temperature measurement, wide temperature ranges of spectral fittings, and accurate static parameters have all contributed to minimise errors.

Discussion

The energy data in Table 2 show a strong dependence on the type of transition metal, a smaller but very significant dependence on the nature of the O_2CR ligand, and a slight dependence on the type of substituent on the pyridine ring.

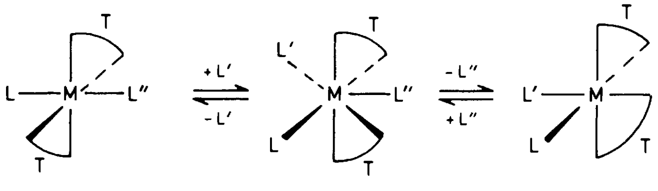
The coalescence temperatures were 30—50 K higher for the Ni^{II} compared to the Co^{II} complexes, and the free energies of activation, $\Delta G^\ddagger$, were accordingly 12—15 kJ mol^{-1} higher for the Ni^{II} complexes. The relatively high magnitudes of these parameters ($\Delta G^\ddagger$ = 50—60 kJ mol^{-1} for Co^{II} and ~70 kJ mol^{-1} for Ni^{II}) reflect the slow isomerisation rates occurring in these complexes. The greater kinetic stability of the Ni^{II} complexes over the Co^{II} complexes is not unexpected[21] and is predominantly a consequence of the greater crystal field stabilisation energy (c.f.s.e.) or molecular orbital stabilisation energy (m.o.s.e.)[22] difference between the (octahedral) ground state and the [trigonal or pentagonal bipyramidal (see later)] transition state for d^8 systems compared to d^7 systems.

The energy data calculated above should be able to provide some insight into the mechanism(s) of the *cis–trans* interconversion process. Ligand replacement reactions of octahedral complexes may be either primarily dissociative (*D*) or associative (*A*) in nature depending on whether a five- or seven-co-ordinative intermediate respectively is formed. However, between these two extreme situations there are dissociative interchange (I_d) and associative interchange (I_a) mechanisms involving interchange of ligands between the inner and next-nearest co-ordination spheres. Nuclear magnetic resonance can provide mechanistic information on such processes from the evaluation of activation parameters such as $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$. Large positive values of these parameters favour a dissociative (*D* or I_d) mechanism. Recent studies by Merbach and co-workers,[23–25] using high pressure n.m.r. measurements, strongly suggested that Co^{II} and Ni^{II} undergo dissociative interchange with non-aqueous solvents (Me_2NCHO, CH_3CN, and CH_3OH) whereas earlier first-row transition elements (*e.g.* Fe^{II} or Mn^{II}) undergo primarily associative interchange. We have suggested earlier[3] that with the $[ML_2T_2]$ ($T = O_2CR$) complexes the most likely mechanism is a dissociative one involving the formation of a five-co-ordinate trigonal bipyramidal L_1 intermediate (see below).



L_2 *trans* L_1 L_2 *cis*

Our $\Delta H^\ddagger$ and $\Delta S^\ddagger$ data now suggest that this view is over-simplistic and that the mechanism depends strongly on the nature of the O_2CR ligands and, to a lesser extent, on the pyridine-type ligand. In $[ML_2T_2]$ (L = 4-alkylpyridine, $T = O_2CCF_3$) large negative $\Delta S^\ddagger$ values imply an essentially associative mechanism (I_a or *A*) of the type shown below. The other associative mechanism[21] involving a square pyramidal intermediate does not lead to isomerisation and can therefore be discounted in the present context. In the mechanism shown a pentagonal bipyramidal intermediate is used for simplicity but it is quite likely that the entering ligand L′ is at an octahedral face.[21] Inspection of Table 2 shows that this associative description appears to be less valid on going from O_2CCF_3 to O_2CCF_2H to O_2CCFH_2 complexes. In other words, as the Arrhenius energies (E_a) or activation enthalpies ($\Delta H^\ddagger$) for the isomerisation increase, the mechanism appears to be more dissociative (I_d or *D*) in nature as previously postulated.[3] This is particularly the case for the cobalt(II) complexes of $O_2CC_2F_5$ and $O_2CC_3F_7$. The predominating type of mechanism will depend in the extreme cases of *D* or *A* mechanisms on the relative amounts of energy required either to rupture a M–L bond to form a five-co-ordinate intermediate or to accept an L ligand into the inner-co-ordination sphere to form a seven-co-ordinate intermediate. No apparent difference in mechanism is observed for analogous complexes of the two transition metals, implying that the metal affects the activation energy but not the mechanism of the isomerisation. Detailed kinetic studies are required to distinguish clearly between the four mechanisms suggested but the present data do provide some insight into the preferred mechanisms, whilst at the same time suggesting that a single exact description of the mechanism of isomerisation valid for this whole series of complexes will not suffice.[26]

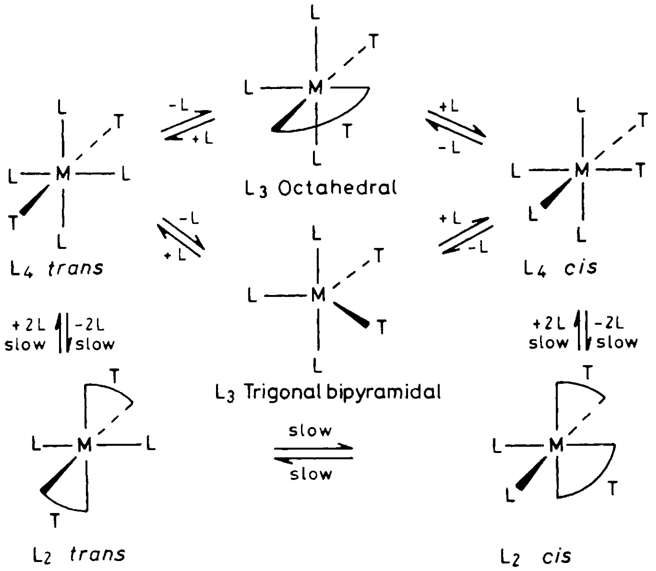


L_2 *trans* L_3 Pentagonal bipyramid L_2 *cis*

The observed trend in $\Delta G^\ddagger$ values is $O_2CC_3F_7 \approx O_2CC_2F_5 > O_2CCF_3 > O_2CCF_2H > O_2CCFH_2$. Now on the basis of anion basicities the relative order of M–O bond strengths will be the exact reverse of this order. Garner and Hughes[27] have commented on the relative lability of M–O_2CCF_3 bonds when reviewing bond-cleavage reactions of metal trifluoroacetates. Also, the unidentate and bidentate abilities of simple carboxylate ions have been shown to decrease with increasing electronegative substitution in the ions.[28,29] Our present results therefore confirm our earlier suggestions[2–4] that the M–O bonds are *not* broken during the L_2 isomerisation since, if they were, an increase in M–O bond strength would be accompanied by an increase in $\Delta G^\ddagger$ values, whereas the opposite trend is observed. The role of the carboxylate ligands therefore appears to be to influence the rates and mechanisms of the replacements of the pyridine-type ligands. This may be viewed in qualitative molecular orbital terms as follows. Stronger M–O bonding will decrease the formal charge on the metal and produce a larger energy difference between the pyridine-type ligand σ orbitals and the metal *d* orbitals. This increased energy difference will result in less mixing of these orbitals and correspondingly weaker M–N bonds, which in turn will enhance the leaving potential of the pyridine-type ligands.

The $\Delta H^\ddagger$ data show a slight dependence on the nature of the pyridine-type ligand such that 4Me-py < 4Et-py < 3Me-py. As these $\Delta H^\ddagger$ values increase, the $\Delta S^\ddagger$ values become more positive implying that the mechanism is becoming more dissociative. These changes are probably a consequence of the slightly different ligand basicities as has been discussed by Kluiber *et al.*[30] when explaining the different rates of ligand (L) exchange with $[NiL_2(acac)_2]$ (acac = acetylacetonate) complexes.

cis–trans isomerism also occurs in the $[ML_4(O_2CR)_2]$ complexes[3] and it is of interest to compare its activation energy with that of the corresponding L_2 complexes. However, dissociation to $[ML_2(O_2CR)_2]$ tends to occur in solution,[11] in the absence of excess ligand L, and an L_4–L_2 equilibrium is quickly established. This complication, plus the fact that the two isomers of the L_4 complexes were in very unequal proportions, precluded any accurate bandshape fittings. An approximate estimate of the energy of the process was, however, obtained from the $\Delta G^{\ddagger}$ value calculated at the coalescence temperature of the complex $[Co(4Me\text{-}py)_4(O_2CCF_3)_2]$. The value of 45 kJ mol^{-1} (Table 2) is markedly lower than any such value for the L_2 complexes, indicating a much more facile isomerism in these L_4 complexes. A dissociative rather than associative process is far more likely here since the latter would require the formation of a seven-co-ordinate intermediate involving seven bulky unidentate ligands which on steric grounds is highly unlikely. A dissociative scheme which can account both for the observed *cis–trans* isomerism and for the presence of two additional species, which do not undergo any exchange processes at low temperatures, is shown below. The two additionally detected species are thus postulated as *cis* and *trans* L_2 complexes by virtue of the expected partial dissociation of L_4 complexes in solution,[11] and their isotropic shifts being very similar to those of the pure L_2 complexes. These L_2 species are only detected at temperatures near band coalescence of the L_4 complexes (*i.e.*, *ca.* 0 to −20 °C) when any *cis–trans* L_2 interconversion or L_4–L_2 interconversion is slow on the n.m.r. time-scale. Hence, their signals remain sharp. On cooling to lower temperatures (*i.e.*, $T < -40$ °C) where *cis–trans* L_4 interconversion is slow, the L_4–L_2 equilibrium appears to have changed even more in favour of the L_4 complexes since the L_2 and accompanying free ligand bands are no longer detectable. The mechanism of the L_4–L_2 interconversion is likely to be purely *D* in nature involving the solvent molecules whereas the *cis–trans* L_4 interconversion probably involves an I_d ligand interchange mechanism with no direct involvement of solvent. The above explanation is somewhat different to that previously suggested[3] but is more in accordance with the additional information now available.



The appreciably lower energies of isomerisation in these L_4 complexes probably reflect the preference of the O_2CR ligands to act as chelates rather than unidentate ligands in octahedral complexes with Co^{II} and Ni^{II}. This confers greater stability on the $[ML_2T_2]$ complexes compared to the $[ML_4T_2]$ complexes at ambient and higher temperatures, as has been seen previously from thermogravimetric studies.[2] However, these more recent studies suggest that at low temperatures (< *ca.* −40 °C) the L_4–L_2 solution equilibrium strongly favours the L_4 complexes.

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