Trifluoroacetate Complexes of Cobalt(II), Nickel(II), and Copper(II) with Pyridine-type Ligands. Part IV.[1] Nuclear Magnetic Resonance Studies of Nickel(II) Complexes and Theoretical Treatment of Spin-density Distributions in Cobalt(II) and Nickel(II) Complexes

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^1H and ^{19}F N.m.r. studies have been carried out on complexes of nickel(II) trifluoroacetate with pyridine and alkylpyridine ligands (L), having stoicheiometries NiL_4T_2 and NiL_2T_2. *cis-* and *trans-*Isomers of these complexes have been detected, although in some cases the chemical-shift distinction is very small. *cis–trans-*Interconversion is slow on the n.m.r. time scale at temperatures < *ca.* 60 °C, in contrast to corresponding Co^{II} complexes. EHMO Calculations have been carried out to determine the conformational preferences of the free ligands and to explain the measured n.m.r. isotropic shifts in both the Co^{II} and Ni^{II} series. The results indicate that the contact shifts are dominated by a σ-delocalisation mechanism but that π-spin polarisation is important particularly for the alkyl-substituent shifts. Limitations of the EHMO method are discussed.

THE previous paper in this series[1] presented a detailed study of n.m.r. spectra of the complexes $[CoL_4T_2]$ and $[CoL_2T_2]$ [$T = CF_3CO_2$; L = py (pyridine), Mepy, or Etpy]. Both series of complexes were shown to be six-co-ordinate and octahedral with the T groups acting as unidentate ligands in the former series of complexes and as bidentate ligands in the latter. *cis–trans-*Isomeric equilibria were detected in all cases and the *cis-trans-*exchange process was followed by variable-temperature studies. Individual isomers were identified at ambient or low temperatures. The present paper discusses n.m.r. results for corresponding Ni^{II} complexes and compares them with the previous results on Co^{II} complexes in terms of different electron-spin delocalisation mechanisms operating in the two cases. An iterative extended-Hückel molecular-orbital (EHMO) treatment[2] has been carried out in an attempt to account for contact shifts

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[1] Part III, P. Anstey and K. G. Orrell, *J.C.S. Dalton*, 1974, 870.

[2] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

in the two series of complexes. For the Co^{II} complexes this was only possible after experimental isotropic shifts had been separated [3,4] into contact and dipolar (pseudo-contact) contributions.

EXPERIMENTAL

The Ni^{II} complexes were prepared as previously.[5,6] N.m.r. spectra were obtained using concentrated solutions of the complexes in $CDCl_3$ (99·8% isotopically pure) and $(CD_3)_2CO$ (99·5% isotopically pure). The majority of the ^1H spectra were obtained using either a Varian HA-100 or a Jeol MH-100 spectrometer, both operating at 100 MHz. The latter instrument was operated in the 'drift mode' as previously described.[1] ^{19}F Spectra were obtained with a Perkin-Elmer R10 spectrometer operating at 56·458 MHz. Referencing of spectra was as for the Co^{II} complexes.[1]

EHMO Calculations were carried out using a modified version of a computer program, kindly supplied by Professor R. S. Drago, on the S.R.C. Atlas computer with a Fortran V compiler. Input consisted of atomic cartesian co-ordinates, details of the atomic orbitals on each atom (1*s* orbitals were omitted for C and N atoms) and of basis orbitals employed, and parameters to produce self-consistent charge by an iterative process.

TABLE 1

^1H N.m.r. spectral data

Complex	Solvent	t/°C	Chemical shifts [a]/p.p.m.					Assignment
			α-H	β-H	γ-H	CH_3	CH_2	
$[Ni(\gamma\text{-pic})_4T_2]$	$CDCl_3$	40	*b*	+25·8		−7·49		*trans*-L_4
			b	+31·1		−9·53, −10·3		*cis–trans*-L_2
		−70	+167	+52·9		−15·8		*trans*-L_4
						−17·6		*cis*-L_4 or *cis–trans*-L_2
	$(CD_3)_2CO$	−90	*b*	+57·4		−17·7		*trans*-L_4
$[Ni(\gamma\text{-pic})_2T_2]$	$CDCl_3$	40	*b*	+31·3		−9·77, −10·6		*cis–trans*-L_2
		−70	*ca.* +180	+50·4		−16·1, −17·6		*cis–trans*-L_2
$[Ni(\gamma\text{-Etpy})_4T_2]$	$CDCl_3$	38	*b*	+31·4		+0·45	−6·67	*trans*-L_4
				+26·2			−8·50, −9·16	*cis–trans*-L_2
		−70	*ca.* +165	+51·7		+0·96	−13·2	*trans*-L_4
				+49·2		+0·24	−14·8	*cis*-L_4 or *cis–trans*-L_2
	$(CD_3)_2CO$	−86	*b*	+52·6		*c*	−13·2	*trans*-L_4
							−14·4	*cis*-L_4 or *cis–trans*-L_2
$[Ni(\beta\text{-pic})_2T_2]$	$CDCl_3$	40	*b*	+34·9	+8·77, +9·61	+4·20		*cis–trans*-L_2
				+23·5	+5·33	+6·87		*cis–trans*-L_1 (?)
		−70	*ca.* +158, +175	+57·3 [d]	+13·3 [e]	+10·8		*cis–trans*-L_2
	$(CD_3)_2CO$	−90	*b*	+61·0, +63·4 [d]	15·3 [e]	+12·0		*cis–trans*-L_2
$[Ni(\beta\text{-Etpy})_4T_2]$	$CDCl_3$	40			very complex			
		−70	*ca.* +177	57·7	13·3	1·48	10·1	*trans*-L_4
				54·7				*cis–trans*-L_2 or *cis*-L_4
	$(CD_3)_2CO$	−85	*ca.* +175	57·9	13·4	(?)	9·95	*trans*-L_4
				56·6				*cis–trans*-L_2 or *cis*-L_4
$[Ni(py)_4T_2]$ $[Ni(py)_2T_2]$	$CDCl_3$	33·5	*ca.* +114	+30·9	+7·66, +8·57			*cis–trans*-L_2 (?)

[a] Shifts relative to diamagnetic ligand values. Positive δ values denote low-field shifts. [b] Unobservably broad. [c] No value obtained due to overlap with solvent band. [d] High-field shoulder attributed to L_1 complex. [e] Low-field shoulder attributed to L_1 complex.

RESULTS AND DISCUSSION

Spectra.—^1H N.m.r. spectral parameters and band assignments are collected in Table 1. Assignments of the bands in Table 1 were fairly unambiguous, being based on relative-intensity measurements and on assignments made for the Co^{II} complexes,[1] where shifts were dominated by σ-contact interaction and generally followed the order α-H ≫ β-H > γ-H > substituent H atoms. Furthermore, relative bandwidths gave a clear indication of the proximity of hydrogen atoms to the central metal ion. The present Ni^{II} complexes showed analogous trends. In a number of cases, however, α-H bands were not detected, presumably due to excessive broadening. Spectra of the complexes $[Ni(\gamma\text{-pic})_4T_2]$ and $[Ni(\gamma\text{-pic})_2T_2]$ (γ-pic = γ-picoline) will be described in some detail and may be taken as fairly representative of the other L_4 and L_2 complexes, with the exception of $[Ni(\beta\text{-pic})_2T_2]$ which will also be considered separately.

$[Ni(\gamma\text{-pic})_4T_2]$. (a) $CDCl_3$ *Solution* (*Figure* 1). At ambient temperature two broad bands were observed for the β-hydrogen atoms and two sharp absorptions (one being a doublet) for the γ-CH_3 hydrogens. On cooling, the bands initially broadened and then sharpened with internal shifts increasing until, at −70 °C, the spectra consisted of a single, somewhat broad, band with a high-field shoulder in the β-H region, a sharp line with a more distinct high-field shoulder in the γ-CH_3 region, and weak sharp bands in the diamagnetic-shift region,

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

[4] W. DeW. Horrocks, *Inorg. Chem.*, 1970, **9**, 690.

[5] Part I, C. A. Agambar and K. G. Orrell, *J. Chem. Soc.* (*A*), 1969, 897.

[6] Part II, C. A. Agambar, P. Anstey, and K. G. Orrell, *J.C.S. Dalton*, 1974, 864.

presumably due to a small amount of free γ-pic. The α-H band (not shown in Figure 1) was observed at −70 °C as a very broad absorption with a very low-field shift (Table 1).

The detection of free-ligand bands indicates that a small amount of decomposition, presumably to $[Ni(\gamma\text{-pic})_2T_2]$ has occurred. Weak bands due to *cis*- and *trans*-isomers of the L_2 complex were indeed observed at all temperatures, indicating that both L_2 *cis–trans* and L_4–L_2-exchange are slow on the n.m.r. time scale even at 40 °C. The free ligand arising from the decomposition must be in rapid exchange with the L_4 complex at higher temperatures. The L_4 complex may consist of unequal abundancies of *cis*- and *trans*-isomers with the latter predominating as in the Co^{II} complexes. However, unambiguous distinction between *cis*- and *trans*-isomers was not possible, even at the lowest temperatures, due either to the small chemical-shift difference between the isomers or to partial or complete overlap of the *cis*-L_4 bands with weak L_2 bands or to both factors. An alternative explanation of the lowest-temperature spectrum is that there has been complete breakdown of the *cis*-L_4 complex to the L_2 complex thus leaving a single set of bands for the L_4 complex. The relative simplicity of the spectrum at −70 °C tends to favour this explanation which is summarised in equations (1) and (2).

$$\underset{\text{(solid)}}{[Ni(\gamma\text{-pic})_4T_2]} \xrightarrow{CDCl_3} cis\text{- and } trans\text{-}[Ni(\gamma\text{-pic})_4T_2] \underset{\text{slow}}{\overset{\text{slow}}{\rightleftharpoons}} cis\text{–}trans\text{-}[Ni(\gamma\text{-pic})_2T_2] + 2\,\gamma\text{-pic} \quad (1)$$

$$trans\text{-}[Ni(\gamma\text{-pic})_4T_2] + n\,\gamma\text{-pic} \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} [Ni(\gamma\text{-pic})_{4-n}(\gamma\text{-pic})_nT_2] + n\,\gamma\text{-pic};\ n = 1\text{—}4 \quad (2)$$

(b) $(CD_3)_2CO$ *Solution.* No new results were obtained but the distinction between the major and minor γ-CH_3 bands was more clear cut.

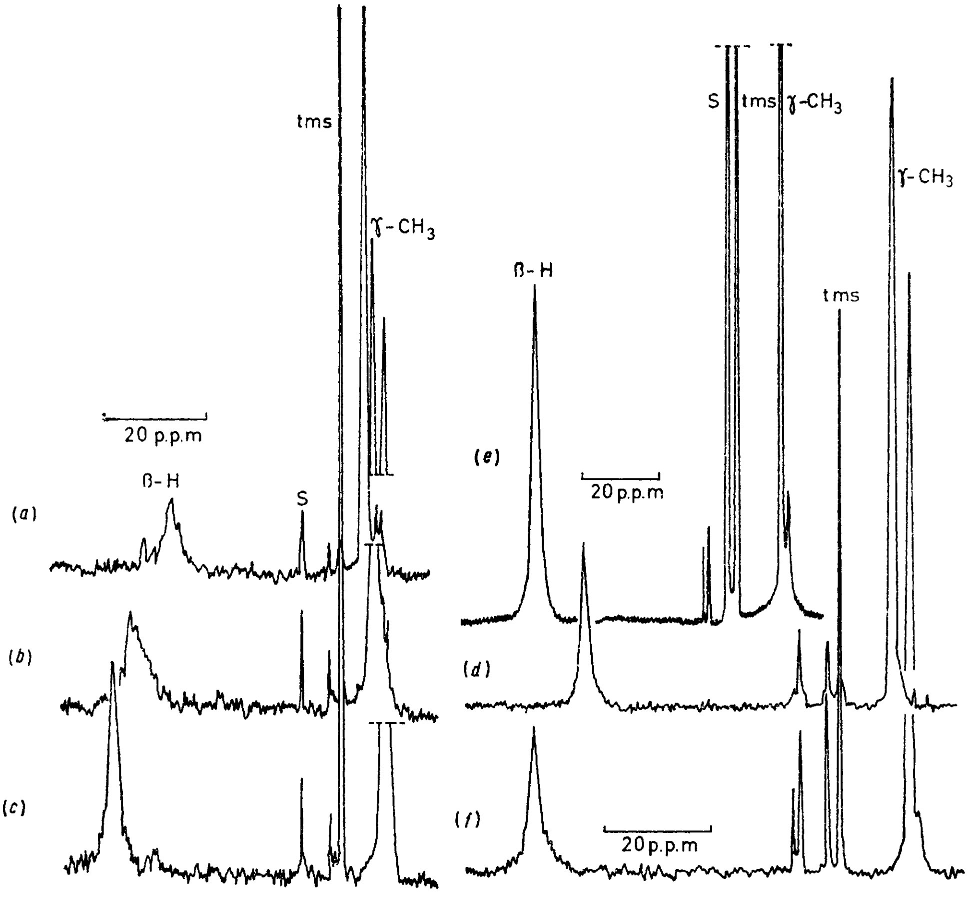

FIGURE 1 N.m.r. spectra of the complex $[Ni(\gamma\text{-pic})_4T_2]$ in $CDCl_3$ at (*a*) 40, (*b*) 20, (*c*) 0, (*d*) −30, (*e*) −48 [in $(CD_3)_2CO$], and (*f*) −70 °C. S denotes $CHCl_3$ or CD_2HCOCD_3 solvent signal

$[Ni(\gamma\text{-pic})_2T_2]$. $CDCl_3$ *Solution* (*Figure* 2). Between 40 and −70 °C the spectra were invariably indicative of *cis*- and *trans*-isomers of approximately equal abundance with isomer exchange being slow on the n.m.r. time scale. The *cis–trans*-isomer distinction was very small (*ca.* 1 p.p.m.) and was only clearly observed for the sharp γ-CH_3 signals. No free-ligand bands were observed, indicating no breakdown to other complex species.

$[Ni(\beta\text{-pic})_2T_2]$ (a) $CDCl_3$ *Solution* (*Figure* 3). This complex behaved somewhat differently from the other L_2 complexes in solution in that free-ligand bands were observed at low temperatures indicating partial breakdown probably to an L_1 species. Such complexes have been isolated in the solid state in the Cu^{II} series [5] so that their detection here is not considered to be too unusual. Unfortunately, distinct bands due to L_1 species were not detected, doubtless due to their partial overlap with *cis*- and *trans*-L_2 bands. However, shoulders on L_2 β-H and γ-H bands at low temperatures may be associated with one or more L_1 complexes. Such complexes may be dimeric or polymeric but, in view of the relative simplicity of the spectra, a dimeric structure involving a single type of ligand environment is favoured. Two likely dimeric structures were considered in the case of Cu^{II} L_1 complexes,[5] but there is insufficient evidence in this case to distinguish between the two possibilities.

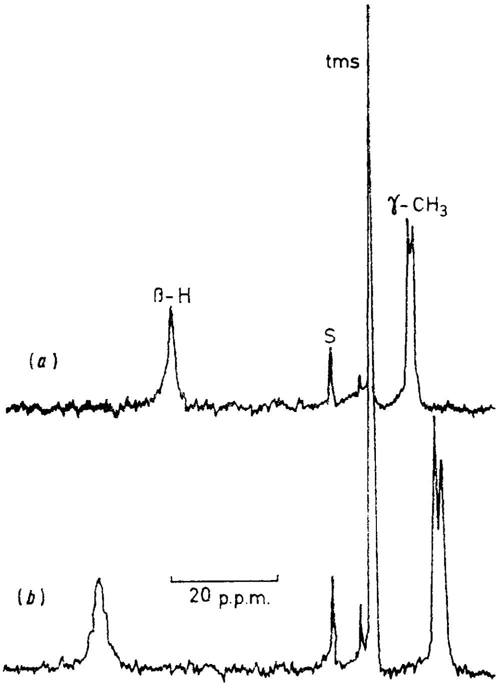

FIGURE 2 N.m.r. spectra of the complex $[Ni(\gamma\text{-pic})_2T_2]$ in $CDCl_3$ at (*a*) 40 and (*b*) −50 °C. S denotes $CHCl_3$ solvent signal

(b) $(CD_3)_2CO$ *Solution*. The spectra in this solvent indicate a somewhat greater preponderance of either the *cis*-L_2 complex or an L_1 complex or both. Isotropic shifts of both these complexes are thought to be virtually identical.

The remainder of the Ni^{II} complexes studied are referred to in Table 1. We conclude from these studies that $[NiL_4T_2]$ complexes exist in $CDCl_3$ solution as *cis*- and *trans*-isomers with one isomer predominating. Steric considerations and electronic-spectral data suggest that the *trans*-isomer predominates. This conclusion was also reached in the case of the Co^{II} complexes where the two isomers were clearly distinguished. In the present Ni^{II} complexes the isomer distinction is not as clear cut, due mainly to the virtual absence of dipolar shifts and partial decomposition in solution of $[NiL_4T_2]$ complexes to $[NiL_2T_2]$. Exchange rates between these isomers are slow on the n.m.r. time scale even at ambient temperatures, this being in obvious contrast to the Co^{II} complexes. All the $[NiL_4T_2]$ complexes underwent a small amount of breakdown to $[NiL_2T_2]$ in both $CDCl_3$ and $(CD_3)_2CO$, the free ligand so produced exchanging rapidly with the L_4 but not apparently with the L_2 complexes at temperatures above *ca.* −30 °C. $[NiL_2T_2]$ Complexes followed similar trends to those of L_4, the main difference being that isomer abundances were more nearly equal as expected on steric grounds (Table 2) and, with the exception of $[Ni(\beta\text{-pic})_2T_2]$, no loss of free ligand in solution was detected.

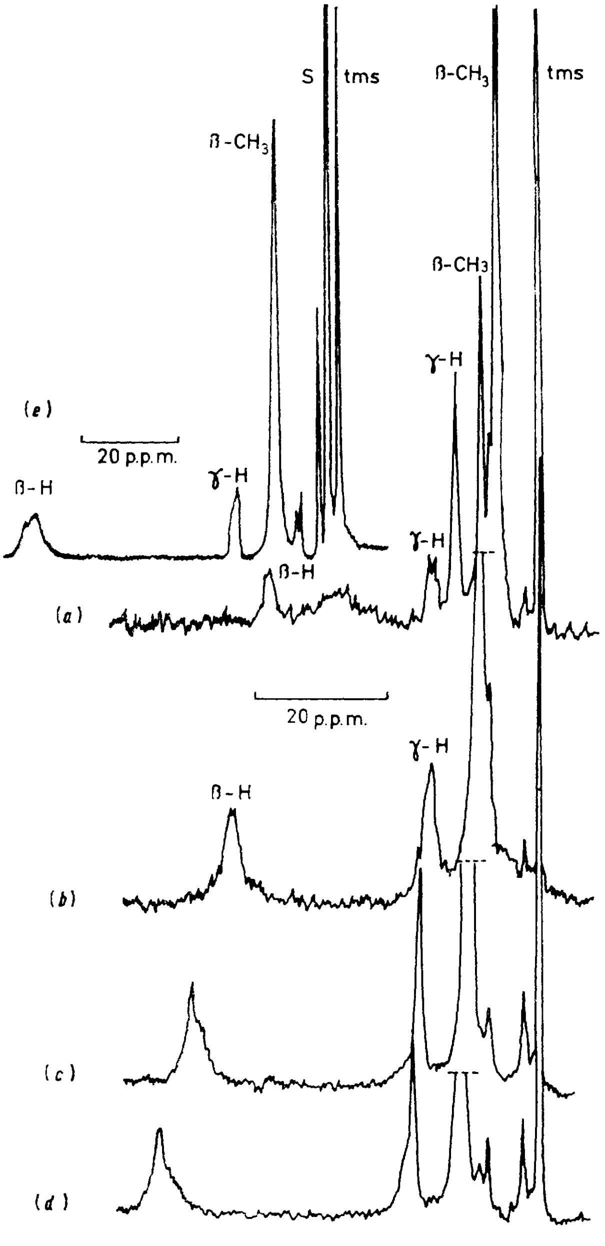

FIGURE 3 N.m.r. spectra of the complex $[Ni(\beta\text{-pic})_2T_2]$ in $CDCl_3$ at (*a*) 40, (*b*) 0, (*c*) −30, (*d*) −50, and (*e*) − 80 °C [in $(CD_3)_2CO$]

^{19}F N.m.r. spectra (Table 2) of the complexes fully support the conclusions of the ^{1}H studies. With some of the L_4 complexes it was not possible to detect the signal of the less-abundant isomer. However, the shift of the detected signal showed a linear Curie-law dependence indicating slow *cis–trans*-exchange at all temperatures up to *ca.* 70 °C. The L_2 complexes, where both isomer bands were observable, showed a similar Curie-law dependence at all temperatures.

TABLE 2

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

Complex [a]	t/°C	Shifts [b]/p.p.m.		Relative intensities
[Ni(γ-pic)$_4$T$_2$]	75	+47	(?)	
	33·5	+52	+98	12 : 1
[Ni(γ-Etpy)$_4$T$_2$]	60	+50	(?)	
	33·5	+53	+98	9 : 1
[Ni(β-pic)$_2$T$_2$]	60	+47	+87	
	33·5	+52	+98	4 : 1
[Ni(β-Etpy)$_4$T$_2$]	80	+44	(?)	
	33·5	+53	+98	4 : 1

[a] In $CDCl_3$ (concn. *ca.* 0·2 mol dm^{-3}). [b] Relative to external CF_3CO_2H ($\delta = 0$). Positive δ denotes low-field shift. Values accurate to ±1 p.p.m. Assignments to individual isomers have not been made.

Before considering a more detailed theoretical treatment of the ^{1}H n.m.r. shifts of the Ni^{II} and Co^{II} complexes, two important differences between the two series should be noted. (1) *cis–trans*-Interconversion rates are appreciably slower for Ni^{II} than for Co^{II} complexes. An accurate comparison of rates cannot be made at present due to complexities of the exchanging spin systems. A very approximate treatment for a typical Co^{II} complex gives an exchange rate constant of *ca.* 10^4 s^{-1} at 33·5 °C; in contrast this rate is not generally attained below 60 °C for the Ni^{II} complexes. This comparison reflects the relative rate constants for H_2O substitution in the inner co-ordination sphere of Co^{2+} and Ni^{2+} at 25 °C, being 1×10^6 and 3×10^4 s^{-1} respectively.[7] (2) The chemical-shift distinction between geometrical isomers of Ni^{II} complexes is an order of magnitude less than that for the Co^{II} complexes. Considering [M(γ-pic)$_2$T$_2$] complexes, $|\gamma\text{-CH}_3(cis)-\gamma\text{-CH}_3(trans)| = 9{\cdot}35$ p.p.m. when M = Co^{II} and 1·5 p.p.m. when M = Ni^{II}. Also, $|\beta\text{-H}(cis)-\beta\text{-H}(trans)| = 17{\cdot}2$ p.p.m. when M = Co^{II} and <1 p.p.m. when M = Ni^{II}. (*N.B.* The Ni^{II} values are based on the assumption that minor bands are due to *cis*-L_4 rather than L_2 species.) This undoubtedly shows how the geometric factor in the dipolar part of the isotropic shifts of the Co^{II} complexes is a highly sensitive probe of the different degrees of distortion from regular octahedral symmetry in the *cis*- and *trans*-complexes. In the Ni^{II} complexes, where no appreciable dipolar shifts are expected by virtue of magnetic isotropy of the *g* factor, *cis–trans*-isomeric distinction is very small and only clearly measurable in a few cases. The distinction is, however, often somewhat greater in $(CD_3)_2CO$ than in $CDCl_3$ solution.

Theoretical Calculations.—EHMO Calculations based on the methods of Drago and his co-workers [8] were carried out on the free heterocyclic ligands β- and γ-picoline and β- and γ-ethylpyridine. Double-zeta orbitals incorporating modified Clementi [9] coefficients of Huzinaga and Arnau [10] were used as basis orbitals. Coulomb integrals were approximated by valence-state ionisation potentials of Hinze and Jaffé [11] and two-centre resonance integrals were computed using the Wolfsberg–Helmholtz arithmetic mean [12] with $K = 1{\cdot}75$. Atomic co-ordinates for significant conformations of the substituted pyridines were based on pyridine co-ordinates used by Clementi [13] together with additional data, namely an aromatic carbon sp^2 orbital radius of 0·070 nm, carbon sp^3 radius of 0·077 nm, and hydrogen 1*s* orbital radius of 0·038 nm.

The EHMO program was first used to study relative energies of the various free-ligand conformations arising from rotation of the methyl and ethyl groups. For β- and γ-picoline, energy calculations indicated that methyl-group rotation was effectively free but, for γ-picoline, the conformer with one methyl C–H bond at right angles to the plane of the heterocyclic ring was slightly more stable (ΔE 84 J mol^{-1}) than the conformer with a C–H bond coplanar with the ring. For β-picoline, the calculations indicated that the relative conformer stabilities were reversed with ΔE 48 J mol^{-1}. It is questionable how much significance should be given to these small energy differences, but a recent analysis [14] of the n.m.r. spectrum of γ-picoline in a nematic phase does support the above conclusion for this ligand. Conformational studies on the ethylpyridine compounds indicate that, whilst rotation of the group as a whole is effectively free, there are a number of conformations which are relatively unfavoured. These tend to be the conformers with the C–C ethane bond coplanar with the ring. Also, conformations with the $-CH_2-$ and CH_3- groups eclipsed are 15—30 kJ mol^{-1} higher in energy than corresponding staggered conformations.

Contact and dipolar shifts. Since only contact shifts are amenable to an EHMO treatment, it was necessary, for the Co^{II} complexes, to separate contact and dipolar contributions and, for the Ni^{II} complexes, to assume negligible dipolar effects. Two seemingly different, but in fact equivalent, methods of separating contact and dipolar shifts are in current use, namely the ratio method of Horrocks [4] and the proportionality method of Zaev and Molin.[3] The latter workers separate the total shift into one portion proportional to the total shift in the analogous Ni^{II} complex, where a pure contact mechanism is assumed, and a dipolar portion proportional to the geometric factor $G(\theta,r)$. Thus, $\Delta\nu_i$ (total, Co^{II}) = $\Delta\nu_i$

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[7] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.

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

[9] E. Clementi, *J. Chem. Phys.*, 1964, **40**, 1944; I.B.M. Tech. Report, RJ-256, 1963.

[10] S. Huzinaga and C. Arnau, *J. Chem. Phys.*, 1970, **53**, 451.

[11] J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1962, **84**, 540.

[12] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, 1952, **20**, 837.

[13] E. Clementi, *J. Chem. Phys.*, 1967, **46**, 4731.

[14] C. L. Khetrapal and A. Saupe, *J. Magnetic Resonance*, 1973, **9**, 275.

$(\text{contact, Co}^{\text{II}}) + \Delta\nu_i\ (\text{dipolar, Co}^{\text{II}}) = K\Delta\nu_i\ (\text{total, Ni}^{\text{II}}) + PG(\theta,r)_i$ where $G(\theta,r)_i = \langle(3\cos^2\theta_i - 1)/r_i^3\rangle_{\text{av.}}$, the average being taken over nuclear motions which are rapid on the n.m.r. time scale; K and P are proportionality constants, the values of which may be obtained by simultaneous solution of a pair of the above equations for two chemically different nuclei in the complex. The values of K and P obtained may be used to predict other shifts in the complex thus giving an internal check on the method. Variation of θ_i and r_i can also be employed within meaningful limits to give the 'best' values of K and P (*i.e.* those which give the most accurate predictions of observed shifts).

For these calculations, the geometry of the heterocyclic ligands was that used for the conformational studies, plus a Co–N bond length of 0·214 nm.[15] Using rotationally averaged geometric factors, the factorising procedure proved satisfactory for *trans*-[Co(γ-pic)$_4$T$_2$] and *trans*-[Co(γ-Etpy)$_4$T$_2$], but for the remaining Co$^{\text{II}}$ complexes the calculated K and P values did not predict a third hydrogen shift well. This was not unexpected for the *cis*-[CoL$_4$T$_2$] complexes where the stereochemistry predicts two non-equivalent types of L ligands with different geometric factors in the absence of any intramolecular ligand exchange. The failure of the factorising procedure for the [CoL$_2$T$_2$] complexes is somewhat surprising in view of its successful use in acac (pentane-2,4-dionate) complexes.[16] One of a number of necessary assumptions [17] in this factorising procedure is that the Co$^{\text{II}}$ complexes have an axially symmetric g tensor. This assumption is almost certainly valid for the *trans*-[CoL$_4$T$_2$] complexes considered here and for complexes like [CoL$_2$(acac)$_2$] where the OCoO angles are closer to 90°. For the [CoL$_2$T$_2$] complexes, with four-membered rings associated with the bidentate CF$_3$CO$_2$ groups, the OCoO angles will be appreciably less than 90° and thus the CoO fragment of the complex may no longer possess C_4 microsymmetry as in the case of [CoL$_2$(acac)$_2$]. In such a situation the more exact dipolar-shift expression of Kurland and McGarvey [18] must be adopted in place of the McConnell and Robertson [19] equation for axial symmetry. However, the former expression applies to rigid ligands, whereas in the present complexes there is evidence both of free rotation about the metal–ligand bonds and of rapid ligand scrambling at all temperatures. The Kurland and McGarvey expression is inapplicable to this situation and, in fact, reduces to the McConnell equation. An alternative explanation for the unsatisfactory factorisation of isotropic shifts into contact and dipolar components is that the assumption of negligible dipolar shifts for the [NiL$_2$T$_2$] complexes may not hold. There have been recent examples [20-22] of Ni$^{\text{II}}$ complexes with appreciable dipolar shifts.

The successful factorising of the *trans*-L$_4$ complexes is shown in Table 3. It should be noted that, for two hydrogen sites per complex, the total predicted shift will be identical with that observed by virtue of the method employed. The validity of the method is indicated in cases where the third shift (α-H shift) is correctly predicted. Whilst this check was not available for (CD$_3$)$_2$CO solutions, K values obtained for the complexes in either solvent were very similar, thus lending support to the method. (CD$_3$)$_2$CO Solutions produced noticeably larger dipolar shifts than those of CDCl$_3$, suggesting a change in either the magnitudes of $g_{\parallel}$ and $g_{\perp}$ or in the molecular geometry of the complex in the two solvents or both.

TABLE 3

Factorisation of *trans*-[CoL$_4$T$_2$] shifts

Ligand		Calculated shifts/p.p.m.			Observed shift/ p.p.m.
		Contact	Dipolar	Total	
γ-pic [a]	α-H	+153	−36·0	+117	+124
	β-H	+48·6	−17·8	+30·8	+30·8 [b]
	γ-CH$_3$	−14·5	−10·7	−25·2	−25·2 [b]
γ-pic [c]	β-H	+47·4	−24·0	+23·4	+23·4 [b]
	γ-CH$_3$	−14·5	−14·5	−29·0	−29·0 [b]
γ-Etpy [d]	α-H	+154	−33·7	+120·3	+120
	β-H	+47·0	−16·6	+30·4	+30·4 [b]
	γ-CH$_2$-	−11·9	−10·0	−21·9	−21·9 [b]
γ-Etpy [c]	β-H	+46·8	−23·2	+23·6	+23·6 [b]
	γ-CH$_2$-	−11·7	−14·0	−25·7	−25·7 [b]

[a] In CDCl$_3$ at −70 °C. [b] Identical with the calculated shifts by virtue of factorisation method. [c] In (CD$_3$)$_2$CO at −70 °C. [d] In CDCl$_3$ at −60 °C.

Electron-delocalisation studies. After averaging over all the energetically favoured conformers of the ligands L, one-electron σ- and π-coupling constants, A_i, were calculated, following previously used methods.[23-25] Table 4 lists these one-electron coupling constants for the Ni$^{\text{II}}$ complexes and Co$^{\text{II}}$ *trans*-L$_4$ complexes for which contact shifts have been deduced. Following Cramer and Drago,[8] scaled combinations of these σ- and π-coupling constants were used to predict experimental A_i values for hydrogen sites other than those used in the scaling procedure. Scaling coefficients found for [Ni(γ-pic)$_4$T$_2$], [Ni(γ-pic)$_2$T$_2$], and [Co(γ-pic)$_4$T$_2$] were retained for the other complexes in their respective series. An examination of Table 4 indicates that σ-delocalisation is the dominant mechanism for the ring hydrogen atoms with the magnitude of the effect tending to fall off with distance from the metal ion. For substituent hydrogen atoms, the shifts may be interpreted primarily in terms of π-spin delocalisation. Table 4 indicates a very variable standard of agreement between experimental and theoretical A_i values.

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[15] I. D. Dunitz, *Acta Cryst.*, 1957, **10**, 307.

[16] W. DeW. Horrocks, R. C. Taylor, and G. N. La Mar, *J. Amer. Chem. Soc.*, 1964, **86**, 3031.

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TABLE 4

One-electron σ- and π-coupling constants and comparison of experimental and calculated A_i values

		$A_i{}^b$/mT			
Complex[a]	H_i	σ	π[b]	Expt.	Calc. (σ + π)
[Ni(γ-pic)$_4$T$_2$]	α-H	1 099	98	50·9	50·9[c]
	β-H	560	165	16·1	25·5
	C_3H	210	−1 569	−4·8	−4·8[c]
[Ni(γ-Etpy)$_4$T$_2$]	α-H	1 082	262	49·6	50·7
	β-H	505	272	15·1	24·2
	CH_2	17	−400	−3·8	−0·7
	CH_3	55	−234	0·3	1·7
[Ni(β-Etpy)$_4$T$_2$]	α-H	1 072	334	52·0	50·5
	α′-H	756	212	?	35·5
	β-H	353	129	17·0	16·7
	γ-H	1 570	277	3·8	73·2
	CH_2	186	−1 692	3·0	2·3
	CH_3	34	−316	0·4	0·4
[Ni(γ-pic)$_2$T$_2$]	α-H	1 099	98	51·4	51·4[c]
	β-H	560	165	13·6	26·6
	CH_3	210	−1 569	−4·7	−4·7[c]
[Ni(β-pic)$_2$T$_2$]	α-H	1 106	480	59·6	53·2
	α′-H	749	92	(?)	35·2
	β-H	350	28	19·3	16·4
	γ-H	1 603	417	4·5	76·0
	CH_3	169	−1 606	3·6	2·1
[Co(γ-pic)$_4$T$_2$]	α-H	733	65	21·4	21·4[c]
	β-H	373	110	6·8	11·1
	CH_3	14	−1 046	−2·0	−2·0[c]
[Co(γ-Etpy)$_4$T$_2$]	α-H	721	175	23·0	21·3
	β-H	337	181	7·0	10·2
	CH_2	37	−156	−1·8	−0·3
	CH_3	11	−267	0·1	0·7

[a] In $CDCl_3$ solution. [b] π-Coupling constants for one unpaired electron delocalised in the highest-filled π-bonding orbital. Values are based on the McConnell equation [24, 25] with $Q = 3·8$ mT for a β-spin as found for the π-anion radical of pyridine. [c] Values identical to experimental values by virtue of the scaling method.

The weakness of the EHMO method, particularly in its inability to handle negative spin densities,[26] have to a large extent been circumvented by recent INDO calculations by Horrocks [27, 28] and Scarlett *et al.*[29] on similar complexes. These calculations, based purely on a σ-delocalisation model, give a superior agreement between calculated and experimental isotropic shifts. Horrocks [28] recently questioned the assumption used both here and by Cramer and Drago that there is *direct* π-spin delocalisation in pyridine-type complexes. However, we feel that this controversy is essentially a semantic one arising from separation of total unpaired-spin densities into σ- and π-symmetries. Whilst the superiorities of the INDO approach are recognised, we feel that the present EHMO calculations give an essentially correct account of the extent and nature of spin delocalisation in these complexes.

We thank Professor R. S. Drago of the University of Illinois for the original EHMO computer program, Dr. C. A. Baker of the P.C.M.U., Harwell, for generous use of 100 MHz n.m.r. facilities, Jeol (U.K.) Ltd for recording some of the earlier 60 MHz spectra, and the University of Exeter for a research scholarship (to P. A.).

[4/101 *Received, 21st January,* 1974]

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