

N.m.r. Studies of the Structures and Bonding of Some Cobalt(II) and Nickel(II) Complexes of Carboxylic Acids

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Some octahedral complexes of types ML_4T_2 and ML_2T_2 , where $M = Co^{II}, Ni^{II}$, $L = \gamma$ -picoline and $T = C_2F_5CO_2, C_3F_7CO_2$ and $CHCl_2CO_2$, have been studied by 1H and ^{19}F n.m.r. spectroscopy. The complexes exist in solution in both *cis* and *trans* isomeric forms, interconversion of the two forms being slow at ambient temperature in the case of the Ni^{II} complexes. The appreciable isomeric distinction shown in the ^{19}F spectra of the acid ligands in contrast to the 1H spectra of the γ -picoline ligands is attributed to a sizeable π -contact interaction of the acid ligands, particularly when they act as bidentate ligands.

Introduction

Some recent studies^{1–2} of complexes of cobalt(II) and nickel(II) trifluoroacetate with pyridine-type ligands have established the existence of *cis-trans* isomeric equilibria in solution. The isomer exchange rates were suitably slow to be followed by low temperature n.m.r. studies. The relatively slow exchange rates are thought to be associated with the coordinating properties of the perfluoroacid ligand as no similar exchange phenomena have been observed in other complexes of stoichiometries $ML_4X_2^{3–4}$ and $ML_2X_2^{5–6}$ where L is a pyridine-type ligand and X is other than trifluoroacetate. On the other hand there is some evidence for the existence of scrambling of acetate-type ligands in the complexes $[Ni(EDTA)]^{2–,7}$ and $[Ni(NTA)_2]^{4–,8}$ (NTA = nitrilotriacetate). In order to examine the effect of mass and size of the acid ligand (T) on the *cis-trans* interconversion rates the n.m.r. spectra of the octahedral complexes ML_4T_2 and ML_2T_2 ($M = Co^{II}, Ni^{II}$, $L = \gamma$ -picoline, $T = C_2F_5CO_2, C_3F_7CO_2, CHCl_2CO_2$) were examined. By studying the trends in the ^{19}F and/or 1H shifts of acid ligand nuclei it was also hoped to derive information concerning the nature of the metal–acid ligand bonding.

Experimental

The complexes were prepared by methods previously described.^{9–10} They were isolated without dif-

ficulty and after washing and/or recrystallisation yielded satisfactory %C, H and N microanalysis figures.

N.m.r. spectra of the complexes were obtained on concentrated solutions in deuteriochloroform (99.8% pure).

Very slight decomposition of the ML_4T_2 complexes to the corresponding ML_2T_2 complexes occurred in this solvent. This could have been eliminated by the presence of excess ligand, L , in the solvent but this somewhat reduced the solubility of the complex. As maximum solubility was essential for studying the ^{19}F spectra this procedure was not followed.

1H spectra were recorded on a JEOL MH-100 100 MHz spectrometer fitted with a standard variable temperature probe. The large sweep widths required for these paramagnetic complexes were accommodated using either the magnetic field drift method previously described¹ or the JEOL wide sweep unit NM-WSI. Sweep widths of up to 300 ppm were obtained by these methods. Spectra were calibrated using the 4 kHz separations of centre band and first lower side band absorptions. All 1H spectra were referenced internally to tetramethylsilane (TMS) and chemical shifts are quoted in δ values ($\delta = 0$, TMS) such that positive values denote low field (high frequency) shifts. ^{19}F spectra were recorded using a Perkin Elmer R10 spectrometer operating at 56.458 MHz. Spectra were referenced relative to external trifluoroacetic acid. Bulk susceptibility corrections were not made as they were considered negligible compared to the magnitude of the shifts detected.

Results

The results of the 1H n.m.r. studies are collected in Table I.

Co(γ -pic)₂T₂ Complexes

At ambient temperatures the spectra consisted of a single set of broad absorption bands for the three types of nonequivalent hydrogens in the γ -picoline ring, the order of magnitude of shifts being α -H \gg β -H $>$ γ -CH₃. The CH₃-hydrogens experience a high field shift in contrast to the ring hydrogens. In the cases of the

TABLE I. ^1H NMR Shift Data.

Complex ^a	Temperature T/°C	Chemical Shifts ^b , δ /ppm			
		α -H	β -H	γ -CH ₃	
Co(γ -pic) ₂ (C ₂ F ₅ CO ₂) ₂	33.5	121 br	32.4, 37.8	-4.4br	
	0	146, 148	35.2, 44.1	-4.4, -8.9	
Co(γ -pic) ₄ (C ₂ F ₅ CO ₂) ₂	33.5	72.4	25.2	-6.4	
	-40	101	34.8	-13.8	
Co(γ -pic) ₂ (C ₃ F ₇ CO ₂) ₂	33.5	122	32.2, 39.4	-2.8, -5.8	
	10	138	34.8, 43.3	-3.1, -7.3	
Co(γ -pic) ₄ (C ₃ F ₇ CO ₂) ₂	33.5	62.6	22.2	-5.0	
Ni(γ -pic) ₂ (C ₂ F ₅ CO ₂) ₂	30	126 br	37.7	-7.6, -8.2	
	-27	149 vbr	44.9	-9.8, -10.6	
Ni(γ -pic) ₄ (C ₂ F ₅ CO ₂) ₂	33.5	?	31.0	-3.0	
	-60	165 vbr	50.1(1), ^c 53.3(5) ^c	-11.7(5), ^c -13.3(1) ^c	
Ni(γ -pic) ₂ (C ₃ F ₇ CO ₂) ₂	30	121 vbr	37.5	-7.3, -8.1	
	-30	161 vbr	46.4	-10.4, -11.4	
Ni(γ -pic) ₄ (C ₃ F ₇ CO ₂) ₂	28	131 vbr	42.8 ^d	-7.4	
	-60	166 vbr	53.6	-11.8	
Co(γ -pic) ₂ (CHCl ₂ CO ₂) ₂	39	α -H 113	β -H 31.2	γ -CH ₃ -6.9	-CHCl ₂ 55.2
	-55	161, 186	29.0, 53.4	-8.1, -21.9	83.2, 91.2
Co(γ -pic) ₄ (CHCl ₂ CO ₂) ₂	25	79.6	23.2	-7.8	66.8
	-60	119	30.7, 47.5	-11.9, -23.4	127
CHCl ₂ CO ₂ H	25	6.06 (-CHCl ₂)	11.84 (-CO ₂ H)		

^a In CDCl₃ solution. ^b Relative to Me₄Si ($\delta = 0$). Positive δ values denote low field shifts. ^c Figures in parentheses denote approximate relative intensities. ^d Band asymmetric with slight high field shoulder presumably due to the minor isomer.

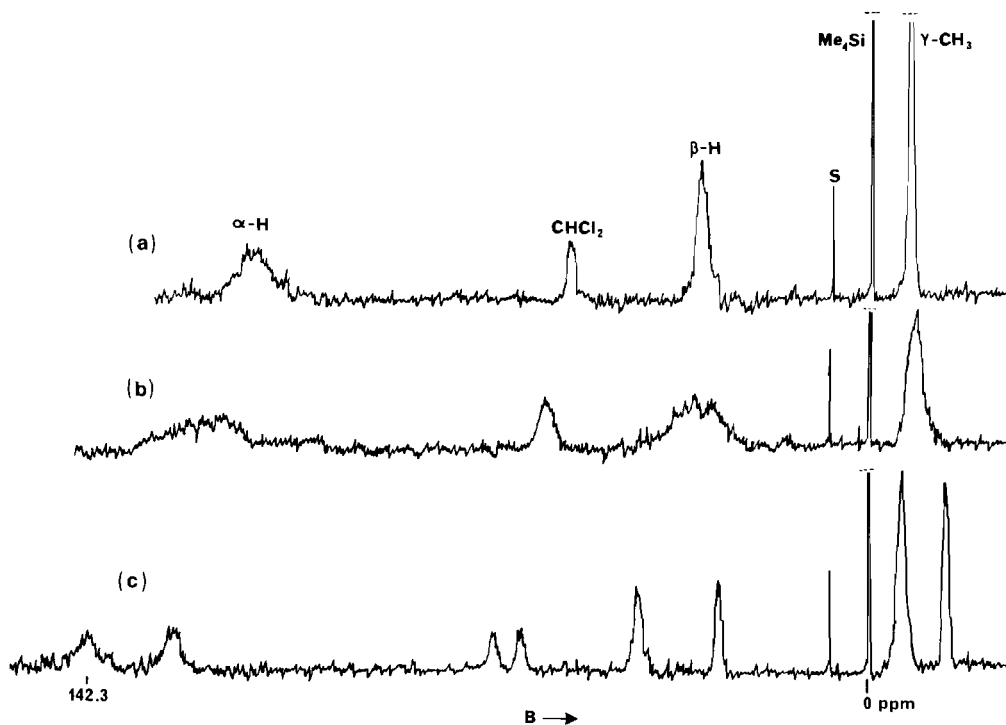


Figure 1. Variable Temperature ^1H NMR Spectra of Co(γ -pic)₂(CHCl₂CO₂)₂ at (a) 39° C, (b) 24.5° C, (c) 0° C. S denotes solvent (CHCl₃) signal.

cobalt(II) perfluoropropionato and perfluorobutyrate complexes partially resolved splitting of the β -H and/or γ -CH₃ bands was observed. This splitting became significantly clearer as the temperature was lowered and at ca. 0° C the spectra of all three complexes consisted of almost equal intensity pairs of bands associated with the α -H, β -H and γ -CH₃ hydrogens. It will be shown that these splittings arise from *cis-trans* isomeric distinction in these complexes at low temperatures. The splittings of the α -H band were surprisingly small in view of the very large isotropic shifts and in fact no splitting was resolved in the case of Co(γ -pic)₂(C₃F₇CO₂)₂. In the spectra of Co(γ -pic)₂(CHCl₂CO₂)₂ (Figure 1), the -CHCl₂ hydrogen exhibits the same behaviour as the γ -picoline hydrogens, being a singlet at room temperature and splitting into two almost equal intensity lines by ca. 0° C.

Co(γ -pic)₄T₂ Complexes

The spectra of these complexes showed the same general trends as the bis γ -picoline complexes with the following important differences: a) It was necessary to cool the complexes to ca. -60° C in order to bring about the band splittings, b) The intensity ratio of the resolved pairs of bands was very different from unity and indeed only in the case of Co(γ -pic)₄(CHCl₂CO₂)₂

was the weaker component detected (for the β -H and γ -CH₃ groups). In this complex it is significant to note the large temperature dependence of the -CHCl₂ hydrogen isotropic shift. On cooling the complex this band moves to lower field much more rapidly than the α -H band which it eventually crosses so that at -60° C the -CHCl₂ hydrogen experiences the largest isotropic shift.

Ni(γ -pic)₂T₂ Complexes

These complexes showed similar trends to the corresponding Co^{II} complexes, the main difference being that the magnitude of the low temperature band splitting was smaller by a factor of 3 to 4 and only resolvable in favourable cases. It was never observed in the α -H bands as the latter were exceptionally broad ($\Delta\nu_{1/2}$ = 10-20 ppm).

Ni(γ -pic)₄T₂ Complexes

The band splittings were again small due to the presumed absence of dipolar shifts (see later and ref. 2) and where the splittings were observed (Table I) the bands were of very different relative intensity (*viz.* ca. 5:1).

The ¹⁹F shift data obtained from ambient temperature spectra of the complexes are shown in Table II.

TABLE II. ¹⁹F NMR Shift Data.

Compound	Chemical Shifts ^a /ppm				Isotropic Shifts ^b /ppm	
	CF ₃ -	-CF ₂ -			CF ₃ -	-CF ₂ -
C ₂ F ₅ CO ₂ H	-7.2	-46.0				
Co(γ -pic) ₂ (C ₂ F ₅ CO ₂) ₂	11.5	42.6			18.7	88.6
	13.6	78.6, 91.0			20.8	124.6, 137
Co(γ -pic) ₄ (C ₂ F ₅ CO ₂) ₂	18.4	51.7			25.6	97.7
Ni(γ -pic) ₂ (C ₂ F ₅ CO ₂) ₂	-1.5	8.7			5.7	54.7
	4.7	53			11.9	99
Ni(γ -pic) ₄ (C ₂ F ₅ CO ₂) ₂	-1.0	15.4			6.2	61.4
	CF ₃ -	CF ₃ -CF ₂	-CF ₂ -CO ₂	CF ₃ -	CF ₃ -CF ₂	-CF ₂ -CO ₂
C ₃ F ₇ CO ₂ H	-4.9	-50.0	-43.0			
Co(γ -pic) ₂ (C ₃ F ₇ CO ₂) ₂	-1.3	-27.9	51.4	3.6	22.1	94.4
	3.0		85	7.9		128
Co(γ -pic) ₄ (C ₃ F ₇ CO ₂) ₂	7.0	-21.5	60.6	11.9	28.5	103.6
Ni(γ -pic) ₂ (C ₃ F ₇ CO ₂) ₂	-3.4	-43.2	15.5	1.6	6.8	58.5
		-46.6	61		3.4	104
Ni(γ -pic) ₄ (C ₃ F ₇ CO ₂) ₂	-4.0	-45.9	112	0.9	4.1	54.2
					CF ₃ -	
Co(γ -pic) ₂ (CF ₃ CO ₂) ₂ ^c					90, 141	
Co(γ -pic) ₄ (CF ₃ CO ₂) ₂					99 ^d , 136	
Ni(γ -pic) ₄ (CF ₃ CO ₂) ₂					52 ^d , 98	
Co(γ -Etpy) ₂ (CF ₃ CO ₂) ₂					88, 138	
Co(γ -Etpy) ₄ (CF ₃ CO ₂) ₂					102 ^d , 142	

^a Shifts relative to external CF₃CO₂H. Positive values denote low field shifts. ^b Shifts relative to the appropriate free acid.

^c Data for trifluoroacetate complexes taken in the main from refs. 1 and 2. ^d Major isomer band.

The left hand side of the table gives the chemical shifts of the complexes and the free acids all relative to external $\text{CF}_3\text{CO}_2\text{H}$ whereas the columns on the right hand side show the shifts relative to the appropriate free acids and thus indicate the effects of coordination on the ^{19}F magnetic environments.

The ^{19}F spectra of all the complexes at ambient temperature indicated that the complexes were in the slow exchange limit with regard to isomer distinction and thus no sample cooling was required. All the bands were rather broad ($\Delta\nu_{1/2} = 2\text{--}20$ ppm) and rather difficult to detect. This was particularly true for the fluorines that experienced the greatest shifts, for example the $-\text{CF}_2-\text{CO}_2$ fluorines. As a result of the difficulty of signal detection only the major isomer bands of the ML_4T_2 complexes were detected. The assignments of the bands were straightforward for the perfluoropropionate complexes being based on relative intensity measurements. In the case of the perfluorobutyrate complexes distinction between the CF_3-CF_2- and $-\text{CF}_2-\text{CO}_2$ fluorines was made on the assumption that the shift of the latter group in the $\text{C}_3\text{F}_7\text{CO}_2$ ligand would be somewhat similar to that in the $\text{C}_2\text{F}_5\text{CO}_2$ ligand. It was thought incorrect to base the assignments on an expected attenuation of shifts as the fluorines became more remote from the paramagnetic centre as that pre-supposes the predominant electron delocalisation mechanism.

An examination of the isotropic shifts in Table II reveals a number of interesting and consistent trends:

(i) Fluorines separated by 4 bonds from Co^{II} (*viz.* CF_3CO_2 , $\text{CF}_3\text{CF}_2\text{CO}_2$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2$) experience low field shifts of *ca.* 90–100 ppm for one isomer and 125–140 ppm for the other isomer. The shifts for the corresponding Ni^{II} complexes are *ca.* 50–60 ppm and *ca.* 100 ppm, respectively.

(ii) Fluorines separated by 5 bonds from Co^{II} (*viz.* $\text{CF}_3\text{CF}_2\text{CO}_2$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2$) experience low field shifts of 19–29 ppm for either isomer. For the corresponding Ni^{II} complexes the shifts are 4–12 ppm for either isomer.

(iii) Fluorines separated by 6 bonds from Co^{II} (*viz.* $\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2$) experience relatively small low field shifts in the range 3–12 ppm. For the Ni^{II} complex the shifts are 1–2 ppm.

Discussion

The spectral data contained in Tables I and II give rise to a number of interesting points. The variable temperature ^1H and ambient temperature ^{19}F spectra indicate that in all these complexes there are *cis-trans* isomeric equilibria with isomer interconversion rates being rapid on the ^1H n.m.r. time scale above ambient temperatures. Individual isomers are detected in the ^1H spectra below *ca.* 10°C and are observed at am-

bient temperatures in the ^{19}F spectra. This observation is similar to that found for corresponding trifluoroacetate complexes.¹⁻² With the bulkier perfluoroacid ligands the coalescence temperatures are appreciably higher than in the former series. For example, the coalescence temperatures of the β -H bands in the complexes $\text{Co}(\gamma\text{-pic})_2(\text{CF}_3\text{CO}_2)_2$, $\text{Co}(\gamma\text{-pic})_2(\text{C}_2\text{F}_5\text{CO}_2)_2$, and $\text{Co}(\gamma\text{-pic})_2(\text{C}_3\text{F}_7\text{CO}_2)_2$ are approx. 25°C , 40°C and $> 40^\circ\text{C}$ respectively. The isomer splittings of the β -H bands are quite similar in magnitude for these three complexes and thus the ratios of the coalescence temperatures may be approximately related to the relative magnitude of the activation energies for the *cis-trans* exchange process. In order to obtain more accurate quantitative estimates of these energy barriers, detailed line shape fitting methods are being undertaken.

A striking difference between the ML_4T_2 and ML_2T_2 complexes, which was also observed for the trifluoroacetate complexes¹⁻² is that the isomer abundancies in the former series are very dissimilar (*e.g. ca.* 5:1) whereas in the latter series they are roughly equal. The isomeric distinction in the ^1H isotropic shifts is considerably greater in the case of the Co^{II} complexes than in the Ni^{II} complexes and is thought to arise from the effect of sizeable dipolar shifts in the Co^{II} complexes and their virtual absence in the Ni^{II} complexes. The ^{19}F shift data, on the other hand, provide a very large isomer distinction for both Co^{II} and Ni^{II} complexes (Table III). It will be seen that just as the ^{19}F isotropic shifts attenuate as the number of intervening bonds between the fluorines and the metal increases, so also does the isomer distinction. The interesting exception here is the complex $\text{Co}(\gamma\text{-pic})_2(\text{C}_3\text{F}_7\text{CO}_2)_2$ where there is a measurable distinction between isomers in the CF_3- absorption but not in the CF_3-CF_2- absorption. This suggests that there may be a sensitive relationship between the spin delocalisation mechanism(s) and the conformations of the fluorocarbon chain. Another interesting aspect of the ^{19}F data is

TABLE III. *Cis-Trans* Isomeric Distinction in ML_2T_2 Complexes.

Complex	^{19}F Shift Differences/ppm		
	$-\text{CF}_2-\text{CO}_2$	CF_3-	CF_3-CF_2-
$\text{Co}(\gamma\text{-pic})_2(\text{C}_2\text{F}_5\text{CO}_2)_2$	42.4 ^a	2.1	
$\text{Co}(\gamma\text{-pic})_2(\text{C}_3\text{F}_7\text{CO}_2)_2$	33.6	0	4.3
$\text{Ni}(\gamma\text{-pic})_2(\text{C}_3\text{F}_7\text{CO}_2)_2$	45.5	3.4	0
$\text{Ni}(\gamma\text{-pic})_2(\text{C}_2\text{F}_5\text{CO}_2)_2$	44.3	6.2	

^a Value based on the mean of the two chemical shifts for the low field component of $-\text{CF}_2-\text{CO}_2-$ signal.

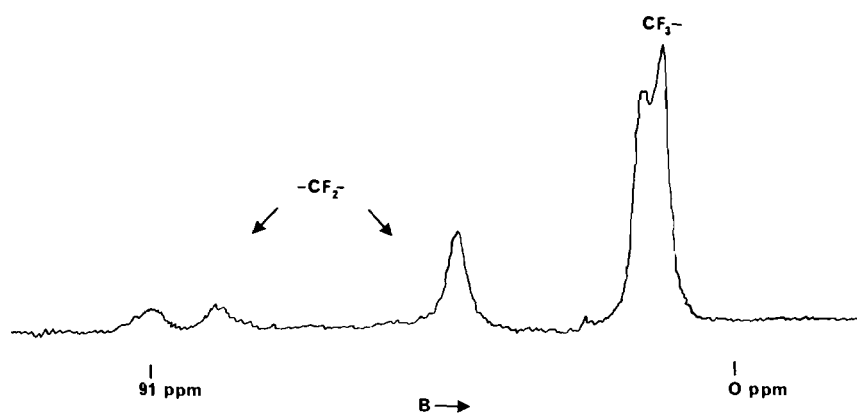
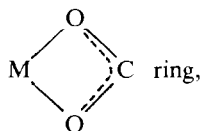


Figure 2. ^{19}F NMR Spectrum of $\text{Co}(\gamma\text{-pic})_2(\text{C}_2\text{F}_5\text{CO}_2)_2$ in CDCl_3 at 33.5°C . Shifts relative to $\text{CF}_3\text{CO}_2\text{H}$ ($\delta = 0$).

the detection of a definite doublet splitting in the lower field component of the two bands associated with the $-\text{CF}_2-\text{CO}_2-$ group of the complex $\text{Co}(\gamma\text{-pic})_2(\text{C}_2\text{F}_5\text{CO}_2)_2$ (Figure 2). The origin of this splitting is somewhat obscure but it points to magnetic non-equivalence of the two $-\text{CF}_2-\text{CO}_2-$ fluorines which might arise either from some conformational preference of the CF_3-CF_2- group with respect to the plane of the



or from the acid ligand being asymmetrically bidentate and involving two different $\text{M}-\text{O}$ and $\text{C}-\text{O}$ bond lengths. If this doublet is attributed to the *cis*-isomer a further possibility* is that the splitting arises from the diastereotopic nature of the fluorines due to the centre of asymmetry on the metal in this isomer.

Perhaps the most important question raised by these ^{19}F and ^1H shift data is regarding the dominant mode(s) of spin delocalisation and/or spin polarisation associated with these acid ligands. Whereas it has been fairly well established¹¹⁻¹² that a ligand such as acetylacetonate (acac) is predominantly involved in π -interaction with a transition metal, the bonding nature of carboxylic acid ligands is far less well understood. It is complicated by the fact that there are five known modes of coordination of such ligands.¹³ In the present complexes, which are known to be monomeric in the solvent used, the acid ligands are monodentate in the ML_4T_2 series and bidentate in the ML_2T_2 series. The striking feature about the ^1H and ^{19}F shifts of the complexed acid ligands is their large low field character. The magnitude of the shifts diminishes as the resonating nucleus becomes more remote from the paramagnetic centre.

* The author is grateful to the referee for this suggestion.

There is no alternation of shift direction for nuclei in adjacent positions which is usually characteristic of π -spin delocalisation. It seems therefore reasonable to suggest that the acid ligands are predominantly involved in a σ -interaction with Co^{II} and Ni^{II} . The absence of any high field shifts can be taken as fairly strong evidence for the dominance of a σ -delocalisation mechanism since some recent studies of some substituted aryl nitroxide π -radicals indicate that with an $n\text{-C}_3\text{F}_7$ substituent although there is no simple alternation of shift direction along the chain both upfield and downfield shifts are detected for the three types of fluorine. The predominance of σ -delocalisation is thought to apply particularly to the ML_4T_2 complexes where T is monodentate. This conclusion is compatible with that reached by Zink and Drago¹⁵ concerning some complexes of type $\text{Ni}(\text{stien})_2\text{T}_2$ (stien = stilbenediamine) where T is monodentate CH_3CO_2 , CH_2ClCO_2 , CHCl_2CO_2 among others. On the basis of i.r. spectral data it was concluded that there was no significant metal-to-ligand π -backbonding. Thus, assuming the same applies to trifluoroacetate complexes one is left with considering ligand-to-metal σ -spin transfer and ligand-to-metal π -spin transfer with the former mechanism predominating.

It should be recognised, of course, that the distinction between σ - and π -mechanisms only strictly applies to regular octahedral complexes where mixing between t_{2g} and e_g orbitals is symmetry restricted. In the present complexes where the symmetry is lower than O_h such distinction is less meaningful. However, electronic spectral data¹⁰ of this class of complexes indicate that any distortions from regular O_h symmetry are relatively small and thus in the ensuing discussion of delocalisation mechanisms the O_h symmetry labels for the orbitals have been retained. Both mechanisms may arise in the high spin Co^{II} complexes but only the former mechanism applies to the Ni^{II} complexes since the metal t_{2g} orbital set is fully filled. In order to account

for the low field shifts it is necessary to provide a mechanism whereby net α -spin (\uparrow) resides in the acid hydrogen or fluorine orbitals. This can arise from a transfer of β -spin (\downarrow) from a filled ligand σ -orbital to a half-filled metal e_g orbital and/or a transfer of β -spin from a filled ligand π -orbital to a half-filled metal t_{2g} orbital.

A comparison of ^{19}F shifts (Table II) of corresponding Co^{II} and Ni^{II} tetrakis γ -picoline complexes shows the latter to be appreciably smaller. This difference may well result from the absence of any ligand-to-metal π -spin transfer since any transfer by this mechanism in the case of the Co^{II} complexes would enhance the net amount of α -spin residing in the fluorine orbitals and thus lead to greater low field shifts.

When one turns to the ML_2T_2 complexes where the acid ligands are bidentate it is necessary to reassess the dominant type of metal-ligand interaction. By analogy with acac-type ligands it seems very reasonable to postulate considerable or possibly dominant π -interaction. This interaction may involve both ligand-to-metal β -spin transfer, as for the CoL_4T_2 complexes, and metal-to-ligand transfer of spin from a metal t_{2g} orbital to a vacant ligand π^* orbital. For the Co^{II} complexes, both direct mechanisms may occur with the metal-to-ligand process involving transfer of α -spin from the half filled metal t_{2g} orbital to a vacant π^* orbital. For the Ni^{II} complexes only the metal-to-ligand process can occur and will involve a net transfer of β -spin from a filled t_{2g} orbital to a vacant π^* orbital by an indirect spin delocalisation or polarisation mechanism.¹⁶ It is significant on inspecting Table II that there is a greater chemical shift distinction of isomers in the ML_2T_2 series than in the ML_4T_2 series. This may be attributed to the greater contribution of direct (and indirect) π -spin delocalisation in complexes involving bidentate carboxylic acid ligands. Support for this conclusion can be found in some studies on substituted phenanthroline complexes¹⁷ where strong evidence was obtained for π -contact shifts being appreciably more sensitive to geometric factors than σ -contact shifts. It is also worthy of note that the isomer distinction is very clear-cut in the ^{19}F spectra of the Ni^{II} complexes in contrast to the ^1H spectra. As dipolar shifts can be neglected as a major cause for this distinction, unlike the Co^{II} complexes, the large isomer distinction must be attributed to a very significant π -contact interaction.

Additional evidence for the essentially different modes of spin delocalisation for nuclei in pyridine-type and carboxylic acid ligands may be adduced in the very different temperature dependences of their respective

absorption bands as evidenced in the complex $\text{Co}(\gamma\text{-pic})_4(\text{CHCl}_2\text{CO}_2)_2$.

More definitive conclusions regarding the nature of the metal-carboxylic acid bonding must await spin density calculations (e.g. INDO type) on these ligands as has been carried out successfully by Scarlett *et al.*¹² on acetylacetonate complexes. The present conclusions may serve for the moment as a qualitative guidance to the interpretation of isotropic shifts of paramagnetic complexes involving carboxylic acid ligands.

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References

- 1 P. Anstey and K.G. Orrell, *J. Chem. Soc. Dalton*, 870 (1974).
- 2 P. Anstey and K.G. Orrell, *ibid*, 1711 (1974).
- 3 D. Forster, *Inorg. Chem.*, 12, 4 (1973); *Inorg. Chim. Acta*, 5, 465 (1973); *ibid.*, 2, 116 (1968).
- 4 I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chim. Acta*, 6, 185 (1972).
- 5 R.W. Kluiber and W. De W. Horrocks, *J. Am. Chem. Soc.*, 87, 5350 (1965).
- 6 E.E. Zaev and Yu.N. Molin, *J. Struct. Chem.*, 7, 639 (1966).
- 7 L.E. Erickson, D.C. Young, F.F.-L. Ho, S.R. Watkins, J.B. Terrill and C.N. Reilley, *Inorg. Chem.*, 10, 441 (1971).
- 8 L.E. Erickson, F.F.-L. Ho and C.N. Reilley, *Inorg. Chem.*, 9, 1148 (1970).
- 9 A.B.P. Lever and D. Ogden, *J. Chem. Soc. A.*, 2041 (1967).
- 10 C.A. Agambar, P. Anstey and K.G. Orrell, *J. Chem. Soc. Dalton*, 864 (1974).
- 11 D.R. Eaton, *J. Am. Chem. Soc.*, 87, 3097 (1965).
- 12 M.J. Scarlett, A.T. Casey and R.A. Craig, *Aust. J. Chem.*, 24, 31 (1971).
- 13 C. Oldham, *Prog. Inorg. Chem.*, 10, 223 (1968).
- 14 J. Goldman, T.E. Petersen, K. Torsell and J. Becker, *Tetrahedron*, 29, 3833 (1973).
- 15 J.I. Zink and R.S. Drago, *J. Am. Chem. Soc.*, 92, 5339 (1970).
- 16 G.N. La Mar in "NMR of Paramagnetic Molecules, Principles and Applications", Editors G.N. La Mar, W. De W. Horrocks, Jr. and R.H. Holm, Academic Press, 1973, Chapt. 3.
- 17 G.N. La Mar and G.R. Van Hecke, *Inorg. Chem.*, 9, 1546 (1970).