Trifluoroacetate Complexes of Cobalt(II), Nickel(II), and Copper(II) with Pyridine-type ligands. Part II.[1] Preparation, Vibrational and Electronic Spectral Properties of Cobalt(II) and Nickel(II) Complexes

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Pyridine, β- and γ-picoline, and β- and γ-ethylpyridine complexes of cobalt(II) and nickel(II) trifluoroacetates have been prepared and fully characterised by spectroscopic methods. All the complexes in the solid state were octahedral and of stoicheiometry ML_xT_2 where L = pyridine-type ligand, T = CF_3CO_2, and x = 2 or 4, with the CF_3CO_2 group being either mono- or bi-dentate. Definitive distinction between these two modes of co-ordination was sought by vibrational and electronic spectroscopy.

We have earlier reported[1] the preparation of some new trifluoroacetate complexes of copper(II) with pyridine-type ligands and have now extended the work to include paramagnetic complexes of cobalt(II) and nickel(II). These transition metals were purposely chosen in order that the complexes might be amenable to high resolution n.m.r. studies.[2] The present paper

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

[2] Part III, P. Anstey and K. G. Orrell, following paper; Part IV, P. Anstey and K. G. Orrell, *J.C.S. Dalton*, 1974, accepted for publication.

describes the preparations, thermal decompositions, and both the electronic and vibrational spectra of these complexes with particular interest being placed on the nature of the co-ordination of the trifluoroacetate ligands.[3]

EXPERIMENTAL

Preparations.—The general method of preparation was to mix a solution of either the hydrated metal trifluoroacetate in 2,2′-dimethoxypropane or the anhydrous metal trifluoroacetate in dry ether solution with the appropriate molar amount of freshly distilled heterocyclic ligand required for the formation of an L_4 or L_2 complex. The resulting mixture was very gently warmed. Excessive heating was avoided particularly when isolation of an L_4 complex was required. The complexes generally precipitated immediately but in a few cases prolonged cooling in ice-water was required. Recrystallisation was often found to be ineffective in improving the purity of the complexes. When increased purity was required the reaction was usually repeated under slightly different conditions, *e.g.* variation of temperature and/or relative amounts of starting materials. The analytical and magnetic susceptibility data are given in Table 1. The pyridine complexes and the tetrakis γ-picoline complexes have been prepared previously[4,5] by similar methods. The magnetic data in Table 1 were obtained by Evans' method.[6] No values are available for the pyridine complexes due to solubility difficulties.

TABLE 1

Analytical data

Complex [a]	Analytical data Required %C	%N	%H	Found %C	%N	%H	$\mu_{eff.}$ [c] / μ_B
$Co(py)_4T_2$	47·90	9·30	3·30	47·1	9·5	3·2	*d*
$Co(py)_2T_2$	37·90	6·32	2·30	36·8	6·8	2·35	*d*
$Co(\beta\text{-pic})_2T_2$	40·76	5·95	2·97	40·9	6·45	2·9	5·0
$Co(\gamma\text{-pic})_2T_2$ [b]	40·76	5·95	2·97	39·0	5·75	2·9	
$Co(\gamma\text{-pic})_4T_2$	51·20	8·50	4·26	51·2	8·65	4·3	5·1
$Co(\beta\text{-Etpy})_2T_2$	43·30	5·60	3·60	41·8	5·8	3·7	4·8
$Co(\gamma\text{-Etpy})_2T_2$	43·30	5·60	3·60	42·6	5·95	3·80	5·0
$Co(\gamma\text{-Etpy})_4T_2$	53·90	7·90	5·10	53·0	8·05	5·1	5·0
$Ni(py)_2T_2$	37·90	6·32	2·30	37·15	6·4	2·6	*d*
$Ni(py)_4T_2$	47·90	9·30	3·30	47·2	9·25	3·45	*d*
$Ni(\beta\text{-pic})_2T_2$	40·76	5·95	2·97	40·05	6·85	3·15	2·9
$Ni(\gamma\text{-pic})_2T_2$ [b]	40·76	5·95	2·97	39·85	6·1	2·95	3·6 (306·5 K)
$Ni(\gamma\text{-pic})_4T_2$	51·20	8·50	4·26	51·15	8·55	4·2	3·2 (306·5 K)
$Ni(\beta\text{-Etpy})_4T_2$	54·05	7·86	5·05	53·95	8·05	4·85	3·2 (306·5 K)
$Ni(\gamma\text{-Etpy})_4T_2$	54·05	7·86	5·05	53·35	8·0	5·1	3·3

[a] Prepared by the addition of the ligand to the metal trifluoroacetate except where otherwise stated. [b] Prepared by thermal decomposition of the corresponding tetrakis ligand complex. [c] Values measured at 278 K except where otherwise stated. [d] Insufficiently soluble.

Thermal Decompositions.—These studies were performed on a number of L_4 complexes using both the vacuum line technique described previously[1] and using a Stanton MF L5 thermobalance. Heating programmes available allowed the furnace temperature to be raised from ambient to *ca.* 1000 °C linearly with time over a period varying from 4 to 24 h.

Analysis.—C, H, and N analyses were carried out using a Hewlett-Packard F & M 185 analyser.

Spectra.—I.r. spectra were recorded in the range 4000—650 cm^{-1} with a Hilger and Watts 'Infrascan' H 900 spectrometer and in the range 850—420 cm^{-1} using a Grubb-Parsons 'Spectromaster' H 2000 spectrometer. The complexes were examined as Nujol and/or hexachlorobutadiene mulls or as potassium bromide discs. No appreciable breakdown of the complexes was detected during disc preparation. Far-i.r. spectra in the range 500—120 cm^{-1} were obtained with a Grubb-Parsons/N.P.L. Cube Mk II interferometer which incorporated a polyethylene terephthalate beam splitter of thickness 3·75 μm and a silicon window Golay detector. Black polyethylene was used to filter out all radiation > *ca.* 550 cm^{-1}. Spectra were computed to a resolution of 5 cm^{-1} using a standard Fourier cosine transformation programme. All complexes were examined as polyethylene discs. Electronic spectra were recorded in the range 190—850 nm on a Pye Unicam SP 1800 spectrophotometer and in the range 800—1300 nm using an Optica CF4NI double beam grating instrument. 1 cm Silica cells were used throughout.

RESULTS AND DISCUSSION

Thermal Decompositions.—A number of the L_4 complexes in Table 1 were thermally decomposed by the vacuum line technique previously described[1] in order to isolate the L_2 complexes. It was generally found that heating *ca.* 2 g of complex for 1 h at 100 °C resulted in a mass loss equivalent to *ca.* 2 pyridine-type ligands per molecule of complex. However, it proved to be most difficult to obtain microanalytically pure samples of L_2 complexes by this method. Further insight into the difficulties were sought by using a thermobalance apparatus for the thermogravimetric studies. Detailed studies were performed on a representative set of four L_4 complexes, namely $Ni(py)_4T_2$, $Ni(\gamma\text{-pic})_4T_2$, $Co(\gamma\text{-pic})_4T_2$, and $Ni(\beta\text{-Etpy})_4T_2$. Previous studies on these complexes had led to $Ni(py)_2T_2$ being obtained pure both by the direct (non-thermal) method and by thermal decomposition from the L_4 complex, $Co(\gamma\text{-pic})_2T_2$ and $Ni(\gamma\text{-pic})_2T_2$ being obtained with difficulty by thermal decomposition on the vacuum line and $Ni(\beta\text{-Etpy})_2T_2$ not being obtained pure by either method.

Thermograms for $Ni(py)_4T_2$ and $Ni(\beta\text{-Etpy})_4T_2$ are shown in Figure 1. The exact shapes of the graphs are dependent on the conditions of the particular run (*e.g.* the heating programme and amount of sample used). However, the main features of distinction between the two thermograms may be clearly seen. For a complete sequential decomposition of an L_4 complex *via* an L_2 species three maxima (maximum rates of mass loss) are expected on the thermograms corresponding to loss of the first pair of pyridine-type ligands, then the second pair and finally decomposition of the metal trifluoroacetate. This sequence was clearly seen only for $Ni(py)_4T_2$ where at one stage a

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[3] C. Oldham, *Progr. Inorg. Chem.*, 1968, **10**, 223.

[4] A. B. P. Lever and D. Ogden, *J. Chem. Soc.* (*A*), 1967, 2041.

[5] S. Amasa, D. H. Brown, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1969, 2892.

[6] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

near-zero rate of ligand loss occurred enabling $\mathrm{Ni(py)_2T_2}$ to be easily isolated. The thermogram of $\mathrm{Ni(\beta\text{-}Etpy)_4T_2}$ may be taken as fairly typical of the other complexes where isolation of the pure $\mathrm{L_2}$ complex was either difficult or impossible. In these cases the minimum rates of ligand loss are still appreciable and it would appear very fortunate that pure samples of $\mathrm{Co(\gamma\text{-}pic)_2T_2}$ and $\mathrm{Ni(\gamma\text{-}pic)_2T_2}$ were obtained by thermal decomposition methods.

Despite the preliminary nature of these thermal decomposition studies no strong evidence was obtained for complexes of other stoicheiometry, *e.g.* $\mathrm{L_1}$ complexes.[1] The present work suggests that the decompositions might proceed according to the scheme:

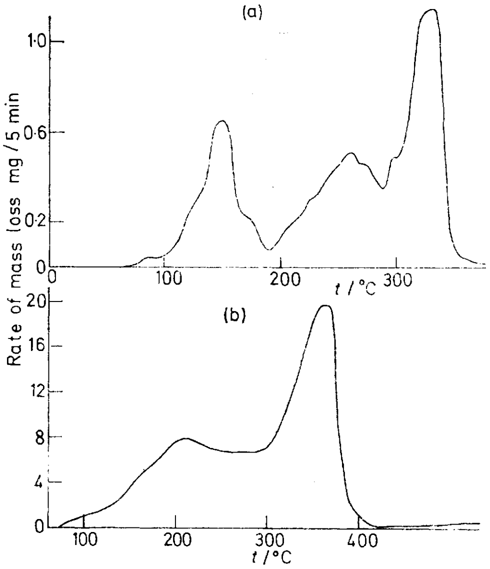

FIGURE 1 (a), Thermogram of $\mathrm{Ni(py)_4T_2}$ using a 12 h heating programme; (b), thermogram of $\mathrm{Ni(\beta\text{-}Etpy)_4T_2}$ using a 4 h heating programme

(i) $\mathrm{ML_4T_2 = ML_2T_2 + 2L}$

(ii) $\mathrm{ML_2T_2 = MT_2 + 2L}$

(iii) $\mathrm{ML_4T_2 = MT_2 + 4L}$

(iv) $\mathrm{MT_2}$ = Residue + volatile products[7]

In the decomposition of $\mathrm{Ni(\beta\text{-}Etpy)_4T_2}$, $\mathrm{Ni(\gamma\text{-}pic)_4T_2}$, and $\mathrm{Co(\gamma\text{-}pic)_4T_2}$, reaction (ii) may be commencing before (i) has been completed and (iii) may be occurring throughout at a slower rate. The decomposition of $\mathrm{Co(\gamma\text{-}pic)_4T_2}$, although performed with a much slower heating programme than the other complexes, showed a significant rate of ligand loss at all times indicating that reaction (iii) may be particularly important in this case. However, for $\mathrm{Ni(py)_4T_2}$, where the rate of ligand loss is virtually zero at one stage, it is suggested that (iii) is negligibly slow and that reactions (i) and (ii) occur approximately sequentially.

Vibrational Spectra.—Near i.r. region. The i.r. data for the trifluoroacetate group vibrations are given in Table 2. The vibrations of the $\mathrm{CF_3CO_2}$ group are distinctly different for the $\mathrm{L_2}$ and $\mathrm{L_4}$ complexes in the following respects.

(i) The difference between the antisymmetric and symmetric C–O vibrations, $(\nu_8 - \nu_3)$, is *ca.* 20—30 cm^{-1} larger for $\mathrm{L_4}$ complexes compared to $\mathrm{L_2}$ complexes. The $(\nu_8 - \nu_3)$ values are comparable with those found by Sharp *et al.*[5] for tetrakispyridine complexes but differ from those of Lever[4] for bispyridine complexes. The source of the discrepancy lies in the assignment of the ν_3 vibrations. Whereas Lever assigned ν_3 around 1350 cm^{-1} we observed no band in this region but assigned ν_3 to a band in the 1455—1450 cm^{-1} region which is absent in the free heterocyclic ligand.

(ii) Probably the most reliable distinctive feature between $\mathrm{L_2}$ and $\mathrm{L_4}$ complexes lies in the changes in the C–F stretching region, 1200—1150 cm^{-1}. For a bidentate $\mathrm{CF_3CO_2}$ group with C_s symmetry, three C–F stretching modes, ν_1, ν_2, and ν_{12} occur[8] with ν_7 and ν_{12} degenerate. The occurrence of only two distinct C–F stretching modes assumes the absence of (i) restricted rotation of the $\mathrm{CF_3}$ groups about the C–C bond, (ii) internal coupling with other $\mathrm{CF_3CO_2}$ groups or other ligands in the complex, and (iii) any asymmetry in the complex. For monodentate $\mathrm{CF_3CO_2}$, the degeneracy of ν_7 and ν_{12} is removed and three bands are expected. This feature was consistently observed for the copper(II) complexes and is further reproduced in all the present cobalt(II) and nickel(II) complexes. Unfortunately, this method of distinction between mono- and bidentate carboxylate groups is limited to halogenoacetates. Higher acid ligands (*e.g.* $\mathrm{C_2F_5CO_2}$ and $\mathrm{C_3F_7CO_2}$)[9] give complex absorption in the C–F stretching region and prevent it from being a diagnostically useful region. For such complexes one must have recourse to far-i.r. spectra for detecting M–O and M–N vibrations.

(iii) One of the $\mathrm{CF_3}$-deformation modes at *ca.* 600 cm^{-1} is consistently larger by 5—15 cm^{-1} for the $\mathrm{L_2}$ complexes compared to the corresponding $\mathrm{L_4}$ complexes.

All the above observations are taken from spectra of solid complexes, either as mulls or potassium bromide discs. A number of $\mathrm{L_4}$ complexes were also examined as solutions in chloroform and some distinct changes were observed. These were explicable in terms of a partial or near complete breakdown of these complexes to the corresponding $\mathrm{L_2}$ complexes. Figure 2 illustrates the change observed for $\mathrm{Ni(\gamma\text{-}pic)_4T_2}$ in the C–F stretching region. Less drastic changes were observed for the $\mathrm{L_2}$ complexes but these were thought to be due either to the differing extents of association in the solid and solution states as suggested by Lever[4] or to different *cis–trans* isomeric equilibria in the two states. Evidence for such equilibria in solution will be presented when the n.m.r. studies are discussed.[2]

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[7] M. J. Baillie, D. H. Brown, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1968, 3110.

[8] R. E. Robinson and R. C. Taylor, *Spectrochim. Acta*, 1962, **18**, 1093.

[9] S. M. Crabtree, R. K. Patient, and K. G. Orrell, unpublished work.

Far-i.r. region (500—120 cm^{-1}). Although spectra were computed to 120 cm^{-1} interpretations were restricted to the main absorption bands which occurred above 200 cm^{-1}.

Although the characteristic metal–oxygen vibrations have been comprehensively reviewed,[10] co-ordinated carboxylato-ligands do not appear to have been investigated in the far-i.r. region apart from a study of the metal salts themselves.[7] The numbers of i.r. active M–N and M–O vibrations were calculated on the basis of the point groups for *cis*- and *trans*-isomers of ML_4T_2 and ML_2T_2 complexes (Table 3). As a first step to interpreting the spectra of the complexes, the spectra of the metal trifluoroacetates were considered. In the region below 450 cm^{-1} there are three main bands which can be unambiguously assigned to $\delta(C-CF_3)$ and $\nu(M-O)$ vibrations (Table 4). Assuming that (a) the $\delta(C-CF_3)$ vibration is fairly insensitive to a variation of M and L throughout the series of complexes, (b) the $\nu(M-N)$ and $\nu(M-O)$ are sensitive to the nature of M, and (c) the expected range of $\nu(Co-N)$ is 200—220 cm^{-1} and of $\nu(Ni-N)$ is 210—240 cm^{-1},[11] the tentative i.r. assignments are given in Table 4.

The L_4 complexes (and the bis β-picoline complex) all produce spectra consisting basically of two multiple bands. The higher wavenumber band is readily assigned to $\delta(C-CF_3)$ and the other is considered to be due to both $\nu(M-O)$ and $\nu(M-N)$. Band shoulders are thought to be due to a minor isomer (probably the *cis*-isomer) being present. The L_2 complexes, except the β-picoline complex, produce a complex band envelope possessing at least four maxima. The $\delta(C-CF_3)$ vibration can be assigned with some confidence but the other assignments are very tentative. The assignments

TABLE 2

Near-i.r. (4000—420 cm^{-1}) data [a]

	L_4 Complexes					L_2 Complexes				
Ligand	ν_8	ν_3	$\nu_3 - \nu_3$	C–F asym, st	CF_3 def	ν_8	ν_3	$\nu_8 - \nu_3$	C–F asym, st	CF_3 def
				Cobalt(II) trifluoroacetate complexes						
py	1710 1693	1425	285 268	1200 1185 1120	604 519	1708	1455	253	1206 1150	609 524
β-pic						1712	1455	257	1205 1147	616 522
γ-pic	1700	1430	270	1200 1168 1131	600 520	1710 1685sh	1455	255	1210 1150	614 523
γ-Etpy	1705	1417	288	1200 1180 1127	600 519	1708	1455	253	1203 1145	613 524
β-Etpy						1703	1455	248	1202 1141	
				Nickel(II) trifluoroacetate complexes						
py	1712 1695	1425	287 270	1205 1185 1130	602 519	1715 1680sh	1450	265	1207 1150	617 606 522
β-pic						1715 1693sh	1455 1460sh	265	1205 1143	616 524
γ-pic	1710 1690	1417	293 273	1200 1170 1130	602 521	1705	1455	250	1200 1148 1133	
β-Etpy	1713	1435	278	1200 1175 1135	604 595 520					
γ-Etpy	1708	1415	293	1200 1170 1125	602 517	1715	1457	258	1208 1148	

[a] All band positions in cm^{-1}.

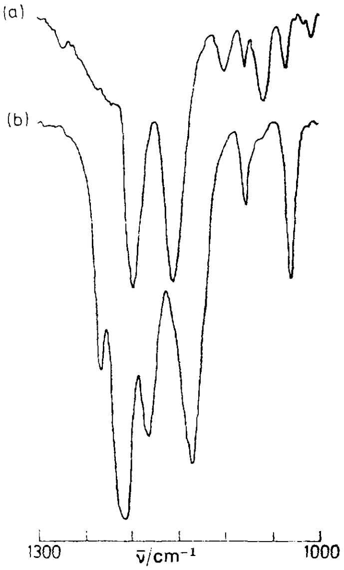

FIGURE 2 I.r. spectra of $Ni(\gamma\text{-}Etpy)_4T_2$ (a), in $CHCl_3$ solution; (b), as KBr disc

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[10] J. R. Ferraro, 'Low Frequency Vibrations of Inorganic and Co-ordination Compounds,' Plenum Press, New York, 1971, ch. 5.

[11] Ref. 9. ch. 7, section 7.5.

TABLE 3

I.r. active vibrations in ML_4T_2 and ML_2T_2 octahedral complexes

Type	Stereochemistry	Symmetry group	ν(M–N)	Number I.r. active	ν(M–O)	Number I.r. active
ML_4T_2	*trans*-oct	D_{4h}	$A_{1g} + B_{1g} + E_u$	1	$A_{1g} + A_{1u}$	1
ML_4T_2	*cis*-oct	C_{2v}	$2A_1 + B_1 + B_2$	4	$A_1 + B_1$	2
ML_2T_2	*trans*-oct	D_{2h} *	$A_g + B_{1u}$	1	$A_g + B_{1g} + B_{2u} + B_{3u}$	2
ML_2T_2	*cis*-oct	C_2 *	$A + B$	2	$3A + 2B$	4

* Applies to both monomeric and polymeric forms.

TABLE 4

Far-i.r. bands/cm^{-1}

	ν(M–N) and/or ν(M–O)	ν(M–O)	δ(C–CF$_3$)	Ring deformation: Complexed	Ring deformation: Free ligand	Other bands
NiT_2	227	325	292			
$Ni(py)_4T_2$	228 242 †	268	278 285	432	407	149 174 423 440 460
$Ni(\gamma\text{-}Etpy)_4T_2$	234		277	500	492 400 422	139 327 410 455
$Ni(\beta\text{-}Etpy)_4T_2$	225 231		282	422	400 420 487	143 496
$Ni(\gamma\text{-}pic)_4T_2$	222		276	489	486 428	153 405 460
$Ni(\beta\text{-}pic)_2T_2$	236		281 295	415	399 454 485	359 435
$Ni(py)_2T_2$	228 246	268	285	432 436	407	160 173 467
$Ni(\gamma\text{-}pic)_2T_2$	215 240		287	484	486 428	441 460
CoT_2	223	320	285			
$Co(\gamma\text{-}pic)_4T_2$	207 213	256	271	488 495	486 428	149 400 445
$Co(\gamma\text{-}Etpy)_4T_2$	216		272	500	492 400 422	456
$Co(\beta\text{-}pic)_2T_2$	207 220		278	407 413 456	399 454 485	442
$Co(\gamma\text{-}Etpy)_2T_2$	230 *		285	445	422 400 492	475
$Co(\beta\text{-}Etpy)_2T_2$	208 222	254	287	413 433 468	400 420 487	—
$Co(\gamma\text{-}pic)_2T_2$	194 203 227 236	251	282	492	486 428	409 445 471

* Poor quality spectrum, evidence of other bands in this region. † Amasa *et al.* (ref. 5) found ν(M–N) for this complex at 248 cm^{-1}.

TABLE 5

Electronic spectra of the cobalt complexes (λ/nm, σ/cm^{-1})

Complex	Solvent	Notes	λ_1	λ_3	σ_1 $^4T_{2g} \leftarrow {}^4T_{1g}$	σ_3 $^4T_{1g}(P) \leftarrow {}^4T_{1g}$	Dq/cm^{-1}	B/cm^{-1}	β (B' = 1115 cm^{-1})
$Co(\beta\text{-}pic)_2T_2$	$CHCl_3$		1250	512	8000	19 531	915	844	0·76
$Co(\beta\text{-}pic)_4T_2$	$CHCl_3$ + β-pic	*a*	1176	501	8500	19 960	964	846	0·76
$Co(py)_2T_2$	$CHCl_3$		1149	507	8700	19 724	988	813	0·73
$Co(py)_4T_2$	Inadequately soluble								
$Co(\gamma\text{-}Etpy)_2T_2$	$CHCl_3$		1227	507	8150	19 724	933	848	0·76
$Co(\gamma\text{-}Etpy)_4T_2$	γ-Etpy		1152	501	8680	19 960	986	828	0·74
$Co(\gamma\text{-}Etpy)_4T_2$	$CHCl_3$		1152	504	8680	19 841	982	818	0·73
$Co(\gamma\text{-}pic)_4T_2$	$CHCl_3$		1155	510	8658	19 608	987	806	0·72
$Co(\gamma\text{-}pic)_4T_2$	Me_2CO	*b*	1157	518	8643	19 305	972	784	0·70
$Co(\gamma\text{-}pic)_2T_2$	$CHCl_3$		1227	510	8150	19 608	934	842	0·76
$Co(\beta\text{-}Etpy)_2T_2$	$CHCl_3$		1170	508	8547	19 685	972	820	0·74
$Co(\beta\text{-}Etpy)_4T_2$	$CHCl_3$ + β-Etpy	*a*	1169	500	8550	20 000	977	842	0·76

[a] Indicates that the L_4 complex is predominant when an excess of L is present. [b] Indicates that L_4 complex is retained in acetone, contrary to Lever's contention of breakdown to L_2 (ref. 4).

TABLE 6

Electronic spectra of the nickel complexes (σ/cm^{-1})

Complex	Solvent	σ_1 $^3T_{2g} \leftarrow {}^3A_{2g}$	σ_2 $^3T_{1g}(F) \leftarrow {}^3A_{2g}$	σ_3 $^3T_{1g}(P) \leftarrow {}^3A_{2g}$	σ_4 $^1E_g \leftarrow {}^3A_{2g}$	σ_4 *	Dq/cm^{-1}	B/cm^{-1}	C/cm^{-1}	β (B' = 1084 cm^{-1})	β′ (C' = 4831 cm^{-1})
$Ni(py)_2T_2$	$CHCl_3$	9174	15 723	25 974	13 106	13 351	1005	863	3446	0·80	0·71
$Ni(py)_2T_2$	CH_3NO_2		15 823	26 110			1010	867		0·80	
$Ni(py)_4T_2$	$CHCl_3$	9389	15 823	25 974	13 089	13 323	1033	861	3433	0·79	0·71
$Ni(\beta\text{-}pic)_2T_2$	$CHCl_3$	9541	15 823	26 042	13 106	13 342	1020	864	3435	0·80	0·71
$Ni(\gamma\text{-}pic)_2T_2$	$CHCl_3$	9389	15 674	25 840	13 158	13 412	1004	858	3494	0·79	0·72
$Ni(\gamma\text{-}pic)_4T_2$	$CHCl_3$	9514	15 898	26 110	13 158	13 392	1030	866	3450	0·80	0·71
$Ni(\beta\text{-}Etpy)_4T_2$	$CHCl_3$	9578	15 873	26 596	13 228	13 470	992	886	3428	0·82	0·71
$Ni(\gamma\text{-}Etpy)_4T_2$	$CHCl_3$	9842	15 924	26 247	13 158	13 389	1020	871	3434	0·80	0·71
$Ni(\gamma\text{-}Etpy)_4T_2$	CH_3NO_2		16 129	26 455			1052	877		0·81	
$Ni(\gamma\text{-}Etpy)_4T_2$	CCl_4		15 873	26 178			1017	869		0·80	

* Corrected for spin–orbit coupling with σ_3.

in Table 4 are based on a single isomer being present but, in view of the n.m.r. studies, it is quite possible that both *cis*- and *trans*-isomers will be present in appreciable amounts as well as the possibility of both monomeric and polymeric species. Thus, according to Table 3, up to six ν(M–O) and three ν(M–N) bands might be expected. The observed complex absorption is therefore no surprise but it does make detailed assignments very difficult. The anomalous behaviour of the β-picoline complex may be due to dominance of one isomeric species in the solid state. N.m.r. studies have shown that this is certainly the case in solution.

Whilst further work is necessary on a wider range of complexes before band assignments can be more definitive, the present work does show that the L_4 and L_2 complexes have distinctly different spectral characteristics in the 500–200 cm^{-1} region.

Electronic Spectra.—The *d–d* spectra of a few of the present and related halogenoacetate complexes have been investigated by several groups.[5,12] The present work is in broad agreement with earlier work and the relevant data are collected in Tables 5 and 6. The spectra are consistent with octahedral co-ordination. The Co^{II} complexes show two main absorptions (σ_1, σ_3) with the σ_3 band *ca.* 20 000 cm^{-1}, possessing further structure. The transition $^4A_{2g} \longleftarrow {}^4T_{1g}$ (σ_2) was not unambiguously observed but could perhaps be assigned to one of the low energy shoulders of the σ_3 band. The Ni^{II} complexes exhibited the usual three main bands for octahedral complexes with the spin-forbidden transition $^1E_g \longleftarrow {}^3A_{2g}$ (σ_4) also being observed in a number of cases. This transition energy was corrected for spin–orbital coupling with $^3T_{1g}(F) \longleftarrow {}^3A_{2g}$ (σ_2) using the intermediate coupling factor.[13,14] *Dq* and *B* Values for both series of complexes were obtained by the graphical ratio method of Lever.[15]

The complexes were studied in chloroform solution in an attempt to detect bands due to individual *cis*- and *trans*-isomers which are known to exist[2] to approximately equal extents in L_2 complexes but with a preponderance of one isomer in solutions of L_4 complexes. The spectra did not reveal distinct bands due to individual isomers but band shoulders observed particularly on the σ_3 band in Co^{II} complexes and on the σ_2 band in Ni^{II} complexes might be considered to be due as much to isomeric distinction as to the previously suggested reasons.[4] In view of the low values of extinction coefficients for the main visible bands (ε *ca.* 38 l mol^{-1} cm^{-1}) it seems probable that the *trans*-isomer is the dominant species for L_4 complexes in solution since *cis*-octahedral complexes often give quite intense visible absorption ($\varepsilon > 100$ l mol^{-1} cm^{-1}).[16] Comparison of these solution studies with diffuse reflectance studies[17] of Co^{II} complexes shows that in the solid state the main visible absorption band (σ_3) is relatively sharp. This does suggest that the broad structured appearance of this band in solution studies may be due to more than one isomeric species each producing complex absorption due to factors such as spin–orbit coupling and lower symmetry ligand field splitting. Variation of solvent (Figure 3) did show an interesting trend in the change of shape of the σ_2 band of the complex, Ni(γ-Etpy)$_4$T$_2$. For both Co^{II} and Ni^{II} complexes, the *cis*-isomer is expected to be increasingly favoured as the polarity of the solvent is increased. Figure 3 shows that the low energy shoulder of the band becomes more pronounced with increase in solvent polarity, suggesting that it may be associated with the *cis*-isomer and the remainder of the absorption with the *trans*-isomer.

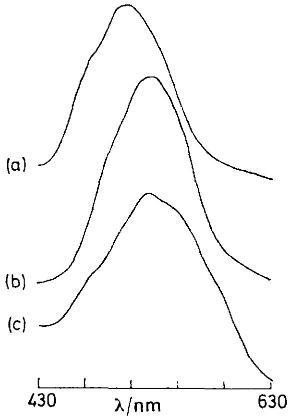

FIGURE 3 Visible electronic spectra of Co(γ-pic)$_4$T$_2$ in (a), CCl$_4$; (b), CHCl$_3$; and (c), CH$_2$NO$_2$ solution

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