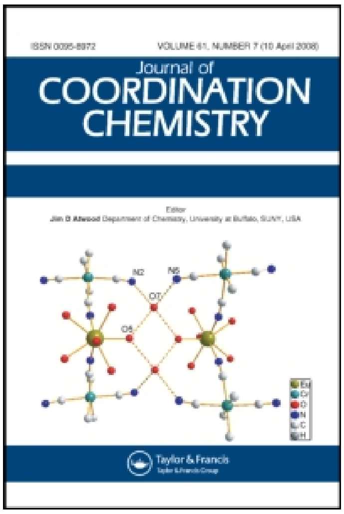

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THIOCARBAMATE COMPLEXES. III. REACTION OF AMINES WITH NICKEL(II) DERIVATIVES

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Solution studies of the reactions of bis(dimethylthiocarbamato)nickel(II) and bis(di-*n*-propylthiocarbamato)-nickel(II) with a variety of primary, secondary, and aromatic amines have been conducted. Primary amines yield either octahedral bis or tetrakis amine adducts, the latter presumably containing monodentate oxygen-bonded thiocarbamate ligands. Normal secondary amines yield bis adducts in equilibrium with a pentacoordinate species, while α-hindered secondary amines yield an anomalous compound of undetermined structure. Aromatic amines yield bis adducts, with the exception of 2,6-lutidine, which exhibits an equilibrium with a pentacoordinate species. The PMR contact shifts and A_i values are reported for the amine protons.

INTRODUCTION

In previous papers from this Laboratory, the synthesis of a variety of complexes having the empirical formula $M(R_2tic)_2$, where R_2tic is an N,N–dialkylthiocarbamate ligand, was reported.[1,2] In the solid state the nickel(II) complexes were formulated as cyclic oligomers in which the nickel atoms are octahedrally coordinated to give $[NiO_2S_4]$ chromophores *via* bridging sulfur atoms; an X-ray crystallographic study of the hexameric n-propyl derivative has confirmed this conclusion.[3] It has been observed, however, that the oligomers fragment when dissolved in a variety of non-coordinating solvents.[1,4] Furthermore, it has been found that the complexes react with pyridine, pyrrolidine and morpholine to give isolable monomeric octahedral adducts of the type $Ni(R_2tic)_2amine_2$.[1,5]

In the present study we have further investigated the interaction of nickel(II) thiocarbamate complexes with amines in order to better establish the nature of the interaction and to compare the behaviour of these compounds with that shown by similar complexes, namely those of dithiophosphate and dithiocarbamate ligands. Recent work by Wasson and co-workers[6,7,8] has rather completely clarified the nature of the reaction between the dithiophosphate complexes and amines. In general it has been found that secondary and sterically hindered aromatic amines react to form five-coordinate adducts, but primary amines give *trans*-octahedral diadducts. The interaction of dithiocarbamate complexes follows a similar pattern, although it is found that the tendency of the dithiocarbamates to form adducts is considerably reduced from that of other 1,1-dithiolates. Details can be found in a review by Coucouvanis.[9] As will be shown below, the N,N-dialkylthiocarbamate complexes of nickel(II) undergo a wider variety of reactions with amines than has been observed previously.

EXPERIMENTAL

Preparation of Compounds and Solutions: The preparation of oligomeric bis(dimethylthiocarbamato)nickel(II) and bis(di-*n*-propylthiocarbamato)-nickel(II) have been previously described.[1] The amines were refluxed over calcium hydride and distilled before use. Amine adducts were prepared for spectral investigations by dissolving the nickel thiocarbamates in a large excess of the neat amine to give solutions *ca.* 10^{-2}-10^{-3} *M* in nickel, except as noted elsewhere. This procedure was chosen so as to maximize the concentration of the most stable adduct. The ratio of metal to amine also was varied in each case so that the possibility of equilibria among various species could be investigated. Several unsuccessful attempts were made to isolate solid adducts of the non-aromatic amines. Evaporation of excess amine in general led to feathery unstable crystals that lost amine or otherwise decomposed when an attempt was made to isolate them as dry solids. Serious attempts to isolate green bis adducts of the aromatic amines were not made, but presumably

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these could be isolated by the use of appropriate synthetic procedures.[1,5]

Spectral Studies: PMR spectra were run on a Varian T-60 Spectrometer operating at 33°C. Tetramethylsilane was employed as an internal calibrant. Assignments of the ligand resonances were taken from standard sources[10] and in some cases were verified by integration. The molar contact shifts for the amine protons were obtained by extrapolation to unit molarity of a plot of chemical shift *vs.* concentration of the nickel complex. In the neat amine solutions there is rapid exchange of the adducted amines and the result is spectral averaging. In the entire concentration range studied for these systems, linearity of the type

$$\nu_{obs} = \nu_d + M\nu_m$$

was observed, where ν_{obs} is the observed chemical shift (Hz) of the uncoordinated amine proton relative to TMS, ν_d is the diamagnetic ligand resonance position, M is the molar concentration, and ν_m is the molar contact shift of the amine protons. The nuclear spin-electron spin hyperfine coupling constant, A_i was evaluated by use of the Bloembergen equation in the following form:[6-8]

$$A_i = -\frac{\Delta\nu_i}{\nu}\,\frac{\gamma_H 3kT}{\gamma_e g\beta S(S+1)}$$

where $\Delta\nu_i$ is the shift difference relative to the diamagnetic ligand (Hz), ν is the probe frequency (Hz), and the other symbols have their usual significance. The value of g was taken as $\mu_{eff}/\sqrt{S(S+1)}$, with μ_{eff} being measured by the Evans method.[11] The measured g values for the complexes studied were 2.16 ± 0.09, a value very similar to that recommended by Angus and Wasson[8] for calculating electron spin-nuclear spin hyperfine coupling constants from the Bloembergen equation.

Electronic spectral studies were carried out on a Cary Model 14 Recording Spectrophotometer, using matched quartz cells (1.0 cm). A quartz spacer was used to obtain path lengths of 0.1 mm, as necessitated by concentrated solutions. Infrared spectra were obtained on a Beckman IR 12 Recording Spectrophotometer. Infrared spectra of certain of the adducts were obtained in neat amine solutions by using KBr liquid cells having a path length of 0.5 mm. Although much of the spectral region was obliterated by amine absorbtions, it frequently was possible to observe two regions of interest, the 1500–1550 cm^{-1} and the metal–ligand regions, with confidence.

All solution spectral studies were made as soon as possible after preparing the solutions since, as has been noted elsewhere,[5c] the thiocarbamate complexes of nickel decompose upon standing for an extended period of time in certain solvents.

RESULTS AND DISCUSSION

Electronic Spectra

Bis(N,N-dimethylthiocarbamato)nickel(II), $Ni(me_2tic)_2$, and bis(N,N-di-*n*-propylthiocarbamato)nickel(II), $Ni(pr_2tic)_2$, were selected for comparative study because they show widely divergent solubility characteristics in non-coordinating solvents that may be indicative of different degrees of molecular aggregation and because it was of interest to determine whether the differences in size of the alkyl groups would be reflected in the reaction with the neat amines. As indicated below, both complexes have been shown to react with a wide variety of amines. However, despite the differences in the alkyl groups, it is now clear that both complexes exhibit about the same adduct-forming ability.

The reaction of 2-picoline with both $Ni(me_2tic)_2$ and $Ni(pr_2tic)_2$ yielded green products having electronic spectra very similar to those of the *bis* adducts formed from pyridine.[1,5] Spectral data are given in Tables I and II. The hypsochromic shift of the $^3A_{2g}\rightarrow{}^3T_{2g}(F)$ (ν_1) transition relative to the pyridine adducts reflects the lower ligand field strength of 2-picoline. The formation of octahedral, presumably *trans*, adducts is in sharp contrast to the reactions of Ni(II) complexes of dithiophosphates, which form predominately five-coordinate adducts with 2-picoline under similar experimental conditions.[7] Consideration of the proposed structures for such adducts suggests a reason for this difference. Where *X* (Figure 1) is a tetrahedrally bonded atom such as phosphorus or arsenic, the addition of a sterically hindered amine results in crowding between R and R′, a downward distortion of the chelate rings, and consequent blocking of the sixth coordination position.[6-8] Where *X* is not a tetrahedrally bonded atom, such as carbon in the thiocarbamate ligand, steric crowding is reduced. In addition the R groups are one atom further removed from the nickel atom. The bis(thiocarbamato)nickel(II) moiety is thus capable of adding two moderately hindered amines. In order to further examine these steric interactions, solutions of the highly hindered amine 2,6-lutidine were studied. These investigations were limited to the propyl derivative, the methyl derivative being

TABLE I

Electronic spectra of the amine adducts of Ni(pr$_2$tic)$_2$, in the neat amines

Amine	molarity x 10^2	Band max (cm^{-1})	Assignment[a]	ε[b]	f x 10^5 [c]
n-propyl	2.52	9,760	ν_1	9	12
		16,500	ν_2	19	25
		26,390	ν_3	38	
isopropyl	2.61	9,130	ν_1	12	14
		15,240	ν_2	23	32
		24,940	ν_3	53	
n-butyl	2.41	9,750	ν_1	10	14
		16,610	ν_2	19	27
		26,670	ν_3	39	
isobutyl	2.22	9,550	ν_1	10	13
		16,310	ν_2	19	27
		26,320	ν_3	40	
D,L-α-methylbenzyl	2.84	9,091	ν_1	12	13
		15,380	ν_2	22	30
		25,000 sh	ν_3	50	
diethyl	2.72	8,640	ν_1	17	19
		11,490 sh		8	
		15,200	ν_2	16	30
		19,050 sh		14	
		23,200	ν_3	37	
di-*n*-propyl	3.08	8,720	ν_1	16	22
		15,340	ν_2	21	
		19,230 sh		19	
		23,260 sh	ν_3	46	
pyrrolidine	2.60	8,580	ν_1	11	
		14,660	ν_2	53	61
piperidine	2.54	8,940	ν_1	14	
		11,490 sh		11	
		14,490	ν_2	31	43
		23,200	ν_3	65	
di-isopropyl	0.77	17,860	see text	160	258
		23,400 sh		71	
2-picoline	2.34	8,880	ν_1	18	21
		11,490 sh		6	
		15,040	ν_2	23	38
2,6-lutidine	2.58	9,140	ν_1	19	22
		11,560 sh		7	
		15,430	ν_2	28	42
2,6-lutidine	11.3	5,880	see text	13	8
		9,710 sh		20	
		10,870 sh		27	
		12,990		63	92
		18,870		38	

[a] $\nu_1 = {}^3A_{2g} \rightarrow {}^3T_{2g}(F)$; $\nu_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$; $\nu_3 = {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, for the octahedral cases. The unassigned shoulders at *ca.* 12,000 cm^{-1} and 19,000 cm^{-1} can be assigned to the spin-forbidden transitions ${}^3A_{2g} \rightarrow {}^1E_g$ and ${}^3A_{2g} \rightarrow {}^1T_{1g}$, respectively, or they might be the result of splitting from one symmetry to a lower one. Similar shoulders are often observed in the spectra of other pseudo-octahedral nickel(II) complexes and assignments of the bands frequently are equivocal (see A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968). Our work does not permit a distinction to be drawn between the two possibilities.

[b] Molar absorption coefficient. Oscillator strengths, calculated only when band shapes and symmetries permitted.

[c] $f = 4.60 \times 10^{-9}\, \epsilon\, \max\, \delta$, where $\epsilon_{\max}$ is the molar absorptivity at the band maximum and δ is the band width at half-height expressed in cm^{-1}. sh = shoulder.

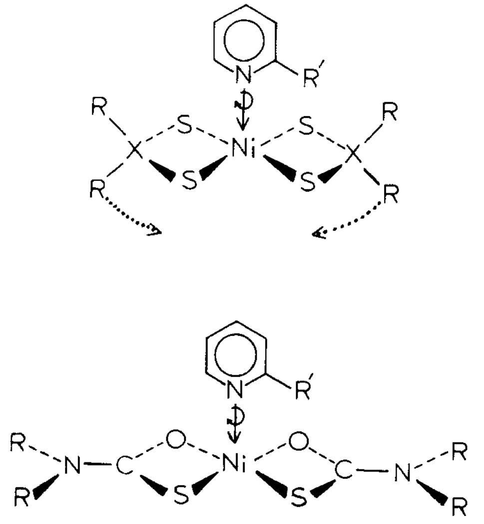

FIGURE 1 Adduct formation. Assume free rotation around Ni–N bond.

insoluble. At low concentrations (~0.03 *M*) green solutions exhibiting optical spectra (Table I) similar to that of the bis pyridine adduct were obtained. At higher concentrations (~0.1 *M*) brown solutions were obtained. Spectral data are given in Table I and the spectrum is shown in Figure 2. The observed color changes were reversible, but efforts directed toward the isolation of the brown complex resulted either in the formation of a green solid or the decomposition of the thiocarbamate complex.

The spectrum of the brown solution can be interpreted in terms of a five-coordinate, distorted square pyramidal adduct. Following the treatment of Furlani and co-workers[12] and assuming C_{4v} symmetry, tentative ligand field assignments for the observed bands are: $^3B_1 \rightarrow {}^3E$, 5,880 cm^{-1}; $^3B_1 \rightarrow ({}^3B_2)^3A_2$, 9,710 cm^{-1}; $^3B_1 \rightarrow {}^3E$, 12,900 cm^{-1}; $^3B_1 \rightarrow {}^3A_2$, 18,870 cm^{-1}. It was not possible to observe the $^3B_1 \rightarrow {}^3E$ transition (expected at *ca.* 21,000 cm^{-1}) because of the high absorbance of this band in 0.1 *M* solutions.

It seems clear that in 2,6-lutidine an equilibrium of the type

$$\mathrm{Ni(pr_2tic)_2(amine) + amine \rightleftarrows Ni(pr_2tic)_2(amine)_2}$$

is established, high concentrations of amine being required to shift the equilibrium toward the bis adduct. This type of equilibrium has not been observed previously in 2,6-lutidine solutions involving the [NiS_4] core. The dithiolates form 1:1 adducts only. These differences undoubtedly reflect the differing steric restraints outlined above for thiocarbamate *vs.* dithiophosphate and similar ligands.

The secondary amines studied may conveniently be divided into two categories: (a) those containing alkyl groups which are normal or branched at the β-carbon or beyond, e.g. diethylamine and di-isobutylamine; (b) those hindered at the α-carbon, e.g. di-isopropyl amine. Amines in the first group react to provide green solutions whose spectral properties are summarized in Tables I and II. These data are clearly indicative of the predominance of octahedral bis adducts, although concentrated (~0.1 *M*) solutions provide spectra which suggest the presence of low concentrations of a five-coordinate species. For example, it is found that in 0.1 *M* solutions of $Ni(pr_2tic)_2$ in di-*n*-propyl amine bands not attributable to octahedral chromophores are found at 13,300 cm^{-1} (shoulder) and 18,190 cm^{-1}. These two bands decrease in relative intensity upon dilution. In the cyclic secondary amines (piperidine and pyrrolidine) bands attributable to five-coordinate chromophores were not observed under any conditions.

It is clear that with normal secondary amines an equilibrium similar to that discussed above is established, but the equilibrium greatly favors the bis adducts. Again by way of contrast, 1:1 adducts (five-coordinate) are strongly favored with dithiophosphate and other [NiS_4] systems.[8] Ciullo and co-workers[13] estimate that the 1:2 diethyl amine adduct of bis(O,O′-diethyl-dithiophosphato)nickel(II) is present in only 71% relative abundance, even at an amine to metal molar ratio of 500. The tendency of the thiocarbamate complexes to form bis adducts again reflects reduced steric interactions relative to the dithiophosphates.

The reaction of $Ni(pr_2tic)_2$ with di-isopropyl amine unexpectedly produced violet solutions over the whole concentration range studied. The electronic spectrum is shown in Figure 2. That the species responsible for the violet color is diamagnetic is indicated by the facts that neither Knight shifts nor paramagnetic line broadening for the amine protons was observed, even in concentrated solutions. Efforts to obtain solid samples of the violet compound have been frustrated by the ease with which amine is lost with reversion to starting thiocarbamate complex, as verified by infrared spectral data. The methyl derivative is insoluble in the neat amine.

The reaction of $Ni(pr_2tic)_2$ with di-isopropyl amine to form exclusively a violet, diamagnetic product further demonstrates the steric specificity with respect to amine. Whether the violet species is in fact planar, perhaps with monodentate thiocarbamate

TABLE II
Electronic spectra of the amine adducts of Ni(me$_2$tic)$_2$, in the neat amines[a]

Amine	molarity x 10^2	Band max (cm^{-1})	Assignment	ϵ	$f \times 10^5$
n-propyl	3.60	9,710	ν_1	10	14
		12,470 sh		2	
		16,530	ν_2	19	27
isopropyl	3.58	9,130	ν_1	11	13
		15,430	ν_2	23	36
n-butyl	3.39	9,780	ν_1	9	13
		16,640	ν_2	19	26
isobutyl	2.96	9,480	ν_1	10	13
		16,310	ν_2	19	27
diethyl	2.73	8,670	ν_1	15	17
		11,470 sh		8	
		15,380	ν_2	19	
		19,050 sh		18	
		23,260 sh	ν_3	45	
dipropyl	3.43	8,640	ν_1	12	13
		11,620 sh		4	
		15,410	ν_2	13	28
pyrrolidine	3.51	8,560	ν_1	11	
		11,630 sh		9	
		14,620	ν_2	39	45
piperidine	3.83	8,810	ν_1	14	16
		11,490 sh		8	
		14,410	ν_2	34	40
2-picoline	1.30	8,850	ν_1	16	18
		11,530 sh		4	
		15,270	ν_2	23	34

[a] See Table I footnotes for explanation of symbols.

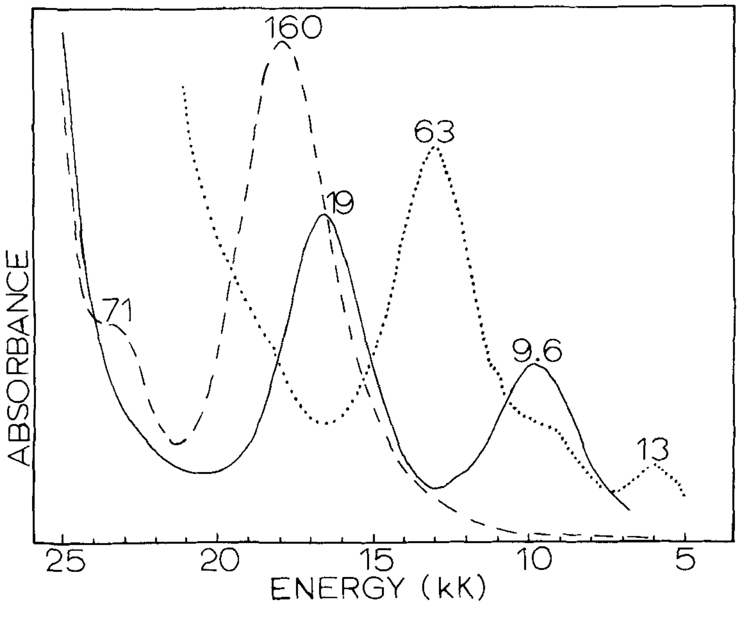

FIGURE 2 Electronic spectra of Ni(me$_2$tic)^2 in *n*-propyl amine (solid line); Ni(pr$_2$tic)$_2$ in di-isopropylamine (dashed); and Ni(pr$_2$tic)$_2$ in 2,6-lutidine, 0.11 M (dotted). (Note arbitrary absorption scale; extinction coefficients noted above main peaks.)

ligands, or is pseudo-octahedral with a sufficiently weak tetragonal ligand field component to permit a singlet ground state has not been resolved.

Reactions of $Ni(me_2tic)_2$ and $Ni(pr_2tic)_2$ with primary amines also are dependent upon substitution patterns at the α-carbon atom. The sterically hindered primary amine D,L-α-methylbenzyl amine provides green complexes whose paramagnetism ($\mu = \sim 2.9$ BM) and electronic spectra (Tables I and II) are essentially identical to those of the other octahedral bis adducts found in the present work and elsewhere.[1] No evidence for pentacoordination was found in this or any of the other primary amines studied.

When treated with straight-chain primary amines the thiocarbamate complexes form paramagnetic ($\mu = \sim 3$ BM) blue compounds, a typical electronic spectrum of which is given in Figure 2. Additional spectral data are given in Tables I and II for a variety of amines. There is no spectral evidence that other species are formed. The magnetic moments and the spectra are characteristic of nickel(II) in an octahedral environment, although it is found that the $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transition undergoes a bathochromic shift on the order of magnitude of $1000\ cm^{-1}$ relative to the green bis-amine adducts discussed above. Comparable shifts occur for ν_2 and ν_3 as well. Again it has not been possible to isolate the blue compounds as solids owing to the ease with which they lose amine. The two most reasonable formulations are octahedral, bis adducts, $Ni(R_2tic)_2(amine)_2$, or octahedral, tetrakis adducts, $Ni(R_2tic)_2(amine)_4$, in which the thiocarbamate moieties are monodentate. Monodentate thiocarbamate ligands, bonded through the sulfur atom, have been identified previously in some zinc(II) complexes of the type $Zn(R_2tic)_2(amine)_2$.[2,14] However, there appear to be no well characterized compounds in the literature which are analogous to the $Ni(R_2tic)_2(amine)_4$ formulation. Ciullo and co-workers[13] described an

TABLE III
Observed PMR contact shifts for the amine adducts of $Ni(pr_2tic)_2$

Amine	Group	Molar chemical shift (Hz)	$\Delta\nu_m$ (Hz)	A_i(G)
diethyl	NH	+2305	+2349	-0.163
	CH_2	-1064	-908	+0.063
	CH_3	-123	-61	+0.004
dipropyl	NH	+3065	+3110	-0.255
	α-CH_2	-1324	-1172	+0.096
	β-CH_2	-105	-18	+0.001
	CH_3	-54.0	0	–
pyrrolidine	NH	+1975	+2131	-0.175
	α-CH_2	-1113	-948	+0.078
	β-CH_2	-209	-114	+0.009
piperidine	NH	+2345	+2446	-0.194
	α-CH_2	-619	-456	+0.036
	β,γ-CH_2	-192	-102	+0.008
2-picoline	α-H	-1421	-910	+0.079
	CH_3	+3	+152	-0.023
	β-H	-765	-341	+0.030
	β-H	-758	-341	+0.030
	γ-H	-446	0	–
n-propyl	NH_2	+3237	+3304	-0.282
	α-CH_2	-1009	-853	+0.073
	β-CH_2	-133	-49	+0.004
	CH_3	-54	0	–
isopropyl	NH_2	+2560	+2628	-0.217
	CH	-1346	-1164	+0.096
	CH_3	-250	-190	+0.016
isobutyl	NH_2	+3622	+3684	-0.301
	CH_2	-1236	-1090	+0.089
	CH	-210	-120	0.010
	CH_3	-52	0	–
n-butyl	NH_2	+3755	+3817	-0.329
	α-CH_2	-1488	-1331	+0.115
	β,γ-CH_2	-187	-108	+0.009
	CH_3	-54	0	

unstable blue compound that resulted from the reaction of bis(O,O′-diethyldithiophosphato)-nickel(II) with large excesses of *n*-butyl amine and postulated the presence of monodentate dithiophosphate ligands. Kuchen and Hertel[15] reported the formation of bis(diethylthiophosphinato)tetrakis-(pyridine)cobalt(II), and their stated formulation implies an oxygen-bonded monodentate system, but no supporting evidence is given.

Solution infrared measurements tend to support the correctness of the formulation $Ni(R_2tic)_2(amine)_4$, with uncoordinated sulfur atoms. This suggestion is based on the observations that the band assigned[1] as ν_{Ni-S} in the parent compounds disappears, a new band assignable to ν_{Ni-N} appears at *ca.* 578 cm^{-1}, a band at 540 cm^{-1} assignable to ν_{Ni-O} in the parent complexes remains unchanged in the amine solutions, and the broad band centered at 1530 cm^{-1}, which has been assigned[1] to a combination of the C–N and coordinated carbonyl stretching frequencies, remains unchanged. The infrared results unfortunately are not unequivocable and at this time we feel that additional study will be required to define accurately the nature of the blue species.

PMR Spectra

Magnetic resonance studies of paramagnetic coordination compounds have become increasingly important in recent years as a probe for investigating structure and reactivity, and the area has been reviewed by several authors.[16] The primary mechanism by which the unpaired spins on octahedral nickel(II) give rise to shifts in ligand proton resonance positions is the Fermi contact interaction, the pseudo-contact contributions being negligible.[17] Proton magnetic resonance molar contact (or Knight) shifts are given in Tables III and IV for various amine adducts studied in the present work. It is clear in all cases that there is interaction between nickel(II) and amine. The N–H

TABLE IV
Observed PMR contact shifts for the amine adducts of $Ni(me_2tic)_2$

Amine	Group	Molar chemical shift (Hz)	$\Delta\nu_m$(Hz)	A_i(G)
diethyl	NH	+2225	+2269	−0.194
	CH_2	−937	−781	+0.067
	CH_3	−102	−40	+0.003
dipropyl	NH	+2999	+3043	0.247
	$\alpha-CH_2$	−1101	−949	+0.077
	$\beta-CH_2$	−96	−9	+0.001
	CH_3	−63	−9	+0.001
pyrrolidine	NH	+2864	+3022	−0.243
	$\alpha-CH_2$	−1476	−1312	+0.106
	$\beta-CH_2$	−224	−129	+0.010
piperidine	NH	+2226	+2327	−0.182
	$\alpha-CH_2$	−619	−457	+0.036
	$\beta,\gamma-CH_2$	−231	−143	+0.011
2-picoline	$\alpha-H$	−1590	−1079	+0.074
	CH_3	−72	+77	−0.005
	$\beta-H$	−848	−424	+0.029
	$\beta-H$	−840	−424	+0.029
	$\gamma-H$	−446	0	–
n-propyl	NH_2	+3021	+3086	−0.246
	$\alpha-CH_2$	−1158	−1003	+0.080
	$\beta-CH_2$	−237	−154	+0.012
	CH_3	−53	0	–
isopropyl	NH_2	+2528	+2595	−0.214
	CH	−1253	−1071	+0.088
	CH_3	−207	−147	+0.012
n-butyl	NH_2	+3557	+3620	−0.313
	$\alpha-CH_2$	−1529	−1372	+0.119
	$\beta'\gamma-CH_2$	−153	−74	+0.006
	CH_3	−54	0	–
isobutyl	NH_2	+3482	+3545	−0.294
	CH_2	−1226	−1080	+0.089
	CH	−153	−62	+0.005
	CH_3	−52	0	–

proton resonances are broadened and shifted upfield, an observation which is very characteristic of amines that coordinate to nickel *via* nitrogen.[8] Thus the general conclusion reached from the electronic spectral studies is substantiated.

Additionally, downfield shifts in C–H proton resonance positions have been observed. For the saturated alkyl amines the sign of the isotropic electron spin-nuclear spin hyperfine coupling constants, A_i, (Tables III and IV) does not change and there is rapid attenuation of the magnitude of the downfield shifts as one progresses down the chain. The magnitude of the contact shifts and of A_i is comparable to that found for other nickel(II) adducts with alkyl amines.[8] These results clearly are consistent with unpaired spin delocalization through the σ system.[17-20]

In the case of the 2-picoline adducts, there is observed a high field shift for the methyl protons. This effect has been observed previously[18,21] and the mechanism of the shift has been the subject of controversy, as outlined recetly by Sun, Grein, and Brewer.[21] Suffice it to say here that the results are consistent with those reported previously.

SUMMARY

The electronic and pmr spectra of a wide variety of amine adducts of $Ni(pr_2tic)_2$ and $Ni(me_2tic)_2$ have been observed. Both square pyramidal and octahedral complexes are formed, depending on the steric requirements of the addendum. In addition, evidence has been found which suggests that certain amines (diisopropyl amine and straight chain primary amines) form unusual adduct complexes which may involve monodentate thiocarbamate ligands. Overall, the reaction of nickel thiocarbamate complexes with amines appears to be more sensitive to the steric properties of the amines than is the case with other similar nickel(II) complexes.

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