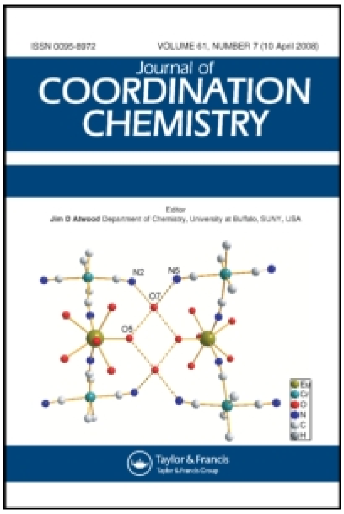

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COMPLEXES WITH SULFUR AND SELENIUM DONORS. V. PROTON NMR AND ELECTRONIC SPECTRA OF AMINE ADDUCTS OF BIS(O,O' DICYCLOHEXYLDITHIOPHOSPHATO)NICKEL(II)

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COMPLEXES WITH SULFUR AND SELENIUM DONORS. V. PROTON NMR AND ELECTRONIC SPECTRA OF AMINE ADDUCTS OF BIS(O,O′-DICYCLOHEXYLDITHIOPHOSPHATO)NICKEL(II)[1]

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N.m.r. contact shifts are reported for a number of mono- and bis-amine adducts of bis(O,O′-dicyclohexyldithiophosphato)nickel(II), Ni(Cyhx–dtp)$_2$. Negative spin densities arising from σ-spin polarization on –NH– and –NH$_2$ protons give rise to large upfield contact shifts whereas positive spin densities are found for protons on carbon atoms adjacent to nitrogen. The electronic spectra of solutions of Ni(Cyhx–dtp)$_2$ in amines are consistent with the formation of five-co-ordinate adducts with secondary amines and six-co-ordinate *trans*-octahedral adducts with primary amines. Spin-delocalization mechanisms, g-values, and electronic spectra are discussed.

INTRODUCTION

The shifts in the nuclear magnetic resonance, n.m.r., spectra of ligands brought about by the presence of paramagnetic ions arise from the coupling of ligand atoms' nuclear spin with unpaired electron density in the paramagnetic ion. The study of paramagnetic or Knight[2] shifts provides a powerful method for mapping the unpaired electron spin delocalization in metal complexes. The theory, interpretation and applications of Knight shifts have been treated in a number of reviews.[3] The mechanisms of spin delocalization onto ligands remain subject to misinterpretation and speculation. In the majority of systems investigated the separation of σ and π contributions to electron spin delocalization has been difficult. Few studies of spin delocalization in complexes in which metal-ligand bonding is essentially of the pure σ-type have been reported.[1, 4–9] Even in σ-bonding systems there is difficulty in sorting out the mechanisms of unpaired electron spin transferral—σ-spin polarization,[4, 5, 6] σ-delocalization[5–11] and hyperconjugative mechanisms.[10, 12] Spin polarization mechanisms leave net antiparallel spin (negative spin density) in adjacent orbitals. Both σ–σ and π–σ spin polarization mechanisms are expected to give rise to alternation of spin densities. In σ-ligand systems the attenuation[7, 11] of the effectiveness of spin polarization is expected to occur rapidly with increasing distance from the paramagnetic ion. Wayland and Rice[4] demonstrated that the protons in ammonia coordinated to copper(II) and nickel(II) in liquid ammonia experience a large upfield contact shift relative to uncoordinated ammonia which is consistent with the σ-spin polarization mechanism. Negative amine proton spin densities have also been observed in nickel(II) amine,[1, 5, 6, 13, 14] aniline,[9, 14] phenylhydrazine and morpholine,[15] and amino acid[7, 8] complexes. In nickel(II) amine complexes the unpaired electrons are in ϵ_g orbitals which are involved in metal-ligand σ bonding. The σ-delocalization mechanisms, whereby unpaired electron spin density is transmitted *via* σ bonds, characteristically gives downfield contact shifts[4–8, 16] which rapidly attenuate with increasing distance from the paramagnetic metal ion. Hyperconjugation mechanisms[12] involving pseudo π-orbitals have been invoked to account for the transfer of spin density from metal[4] and ligand[10] π to ligand σ systems and from ligand σ to ligand π systems.[5]

The present study was undertaken in order to provide additional characterization of the five- and six-coordinate adducts of nickel(II) dithiophosphate complexes. Primary and secondary alkyl amine adducts were chosen since large upfield n.m.r. shifts for protons bound to nitrogen are diagnostic of nickel–nitrogen bonding and correlations of such shifts with ligand basicity could be sought.

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† Abstracted in part from the MS. thesis of J.R.A., University of Kentucky, August, 1971.

EXPERIMENTAL SECTION

Preparation of Bis(O,O′-dicyclohexyldithiophosphato)nickel(II), Ni(Cyhx-dtp)$_2$ Cyclohexanol (112 ml) was added to P^4S_{10} (60 gm) and the reaction mixture stirred until evolution of hydrogen sulfide ceased (Hood!). Nickel(II) acetate tetrahydrate (67 gm) was then added with stirring to the acid obtained from the alcoholysis of phosphorus (V) sulfide[17] and the purple dithiophosphate complex precipitated. The complex was recrystallized from chloroform several times and dried for 24 hours under vacuum (10^{-3} mm Hg) at 42°. Carbon and hydrogen analyses, n.m.r., infrared, and electronic spectra substantiated the identity of complex. Calc'd for $NiS_4P_2O_4C_{24}H_{44}$: 44.66%C; 6.87%H. Found: 44.68%C; 6.71%H.

Electronic spectra were obtained with a Cary Model 14 recording spectrophotometer using matched 1.0 cm quartz cells. Infrared spectra (4000–200 cm^{-1}) were obtained with a Perkin Elmer 621 spectrometer employing Nujol mulls on CsI cells. The proton n.m.r. (pmr) spectra were recorded on a Varian T-60 spectrometer at 35°. Tetramethylsilane (TMS) was employed as an internal standard. Solutions of varying concentration of the adducts (all on the order of 10^{-3} *M* in complex) were prepared by dissolving weighed amounts of Ni(Cyhx-dtp)$_2$ in the neat ligands. This was done in order to maximize the concentration of the preferred adduct[1] and to permit observation of NH proton shifts. Under these conditions the complexes undergo rapid exchange of amine and the concentration dependence of the chemical shift for a particular set of protons obeys the relation:

$$\nu_{obs} = \nu_c M_c + \nu_L$$

where ν_{obs} is the observed chemical shift (relative to TMS), ν_c is the molar shift for the adduct, M_c is the molar concentration of the complex in solution, and ν_L is the chemical shift of the neat ligand. All ν's are in Hz. The molar chemical shift ν_c is defined as that shift which would be observed for a molar solution of the nickel complex. In practice, ν_c is a quantity obtained from extrapolation of a chemical shift *versus* molar concentration plot to unit molarity. The nuclear spin-electron spin coupling constants, A_i, are calculated using the Bloembergen equation:

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

where $\gamma_e/\gamma_H = 6.58 \times 10^2$, $g = \mu_{eff}/\sqrt{S(S+1)}$, $\beta = 9.27 \times 10^{-21}$ ergs/gauss, $S = 1$ for nickel(II), $\Delta\nu$ is the shift relative to the diamagnetic ligand, and ν the probe frequency (both in Hz) and the other symbols have their usual significance. The magnetic moments μ_{eff} were determined by the Evans[19] method.

RESULTS AND DISCUSSION

Ni(Cyhx-dtp)$_2$

The pmr spectrum of Ni(Cyhx-dtp)$_2$ in deuteriochloroform exhibits a strong sharp peak at $\delta = 1.55$ with shoulders at $\delta = 1.83$ and $\delta = 2.00$. $^{31}P - {}^1H$ spin–spin coupling is expected to account for part of the observed pmr band structure. In O,O′-dimethyldithiophosphato complexes with a variety of metal ions J_{POCH_3} was found[20] to be about 16 Hz. The infrared spectrum of Ni(Cyhx-dtp)$_2$ in the region 500–200 cm^{-1} shows one strong and two medium bands at 376, 440 and 355 cm^{-1}, respectively. Metal-sulfur stretching frequencies are found[21] in the range 480–210 cm^{-1} with MS_4 deformation frequencies lying at still lower energies. Comparison of the spectra of bis(O,O′-diethyldithiophosphato)nickel(II) with

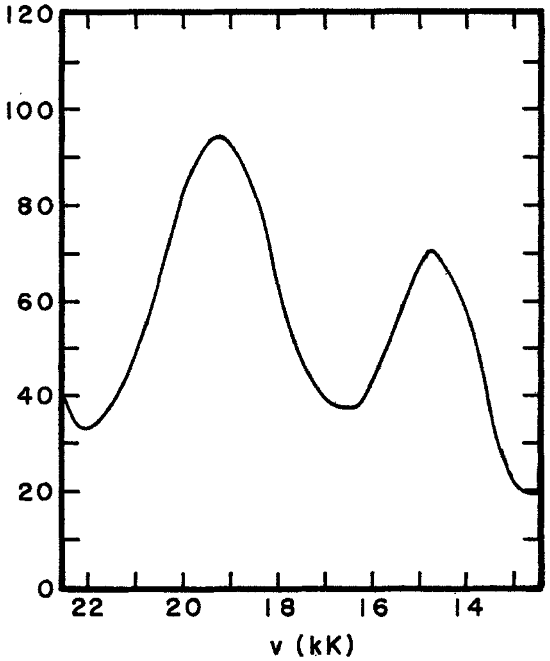


FIGURE 1 Electronic spectrum of Ni(Cyhx–dtp)$_a$ in chloroform.

naturally abundant nickel and ^{62}Ni has shown[23] that νNi—S occurs at 351 cm^{-1}. Infrared and laser Raman studies[22,23] of nickel(II) and other metal dithiophosphate complexes indicate that the metal-sulfur stretching frequencies vary only slightly with change in the hydrocarbon substituent of the ligand. The band at 355 cm^{-1} is assigned to νNi—S with the bands at 440 and 376 cm^{-1} being assigned to ligand deformations. Discussions of the vibrational spectra of dithiophosphate complexes are in preparation.

The electronic absorption spectrum of Ni(Cyhx-dtp)$_2$ is shown in Figure 1 and the energies and oscillator strengths of the transitions are given in Table I. The energies of the antibonding molecular orbitals obtained from atomic d orbitals in square planar transition metal complexes are expected to occur in the sequence $x^2 - y^2 \gg xy > z^2 > xz, yz$.[24] Assuming effective D$_{2h}$ geometry for Ni(Cyhx-dtp)$_2$ leads to the assignments $^1B_{1g} \leftarrow 1A_g$ and $^1B_{3g} \leftarrow {}^1A_g$ for the bands at 14,500 and 19,200 cm^{-1}, respectively. The assignment of the third band at 26,970 cm^{-1} to the $^1A_u \leftarrow {}^1A_g$ transition is consistent with the assignments for $Ni(MNT)_2^{2-}$ (MNT=$S_2C_2(CN)_2^{2-}$)[25] and the observed extinction coefficient and oscillator strength agrees with the expected metal → ligand charge transfer character of the transition. A very strong absorption ($\epsilon_{max} > 10^4$) is also observed at 31,250 cm^{-1}. The origin of this band has not been unambiguously identified but probably arises from an intraligand transition.

TABLE I

Electronic spectra of Ni(Cyhx-dtp)$_2$ in various solvents

Solvent	ν_1 (cm^{-1})	ϵ_{m1}[a]	f_1[b] × 10^6	ν_2 (cm^{-1})	ϵ_{m2}	f_2 × 10^6
chloroform[c]	14,700	35	94	19,200	47	158
Octahedral complexes						
n-propylamine	9,660	6	990	16,500	20	229
isopropylamine	9,220	6	86	14,700	23	359
2-phenylethylamine	9,950	6	64	16,950	16	246
Five-coordinate complexes						
diethylamine	14,100	16	214	23,800	69	1260
morpholine	14,100	36	583	22,600	85	1480
pyrrolidine	15,000	23	367	27,100	96	1330
piperidine	14,700	30	906	22,200	63	1220
N-methylpiperidine	14,800	—	—	24,400	—	—
2-methylpiperidine	14,900	5	159	22,400	111	205
3-methylpiperidine	14,900	34	1220	22,400	71	1320
4-methylpiperidine	14,800	33	997	22,300	69	1280

[a] Molar absorption coefficient.

[b] Oscillator strengths, f, were calculated using the expression $f = 4.60 \times 10^{-9}\epsilon_{max}\nu_{1/2}$ where ϵ_{max} is the molar absorptivity of the band maximum and $\nu_{1/2}$ is the band width at half-height expressed in wave numbers: C. J. Ballhausen, *Progr. Inorg. Chem.*, **2**, 251 (1960).

[c] $\nu_3 = 26{,}970$ cm^{-1}, $\epsilon_m = 695$, $f_3 = 105 \times 10^{-3}$; $\nu_4 = 31{,}250$ cm^{-1}.

ELECTRONIC SPECTRA OF ADDUCTS

The electronic spectrum of Ni(Cyhx-dtp)$_2$ in neat n-propylamine is shown in Figure 2 and is consistent with the *trans*-octahedral structure proposed for the amine adduct. The spectrum is characteristic of the green bis-amine adducts of nickel dithiophosphates[1,15,23,26-30] and other complexes[31] with sulfur ligands. To a first approximation Ni(Cyhx-dtp)$_2$ adducts with primary amines can be treated as having octahedral geometry. Employing the "rule of average environment" and the data of Drago and co-workers[32] for $Ni(n\text{-}C_3H_7NH_2)_6^{2+}$ a value of 10 Dq = 9570 cm^{-1} for Cyhx-dtp is obtained. For the isopropylamine adduct a smaller value of 9090 cm^{-1} is obtained. In a study of the pyridine and picoline adducts[1] of bis(O,O'-isopropyldithiophosphato)-nickel(II), 10 Dq was found to be 8580 cm^{-1} for the thiophosphate

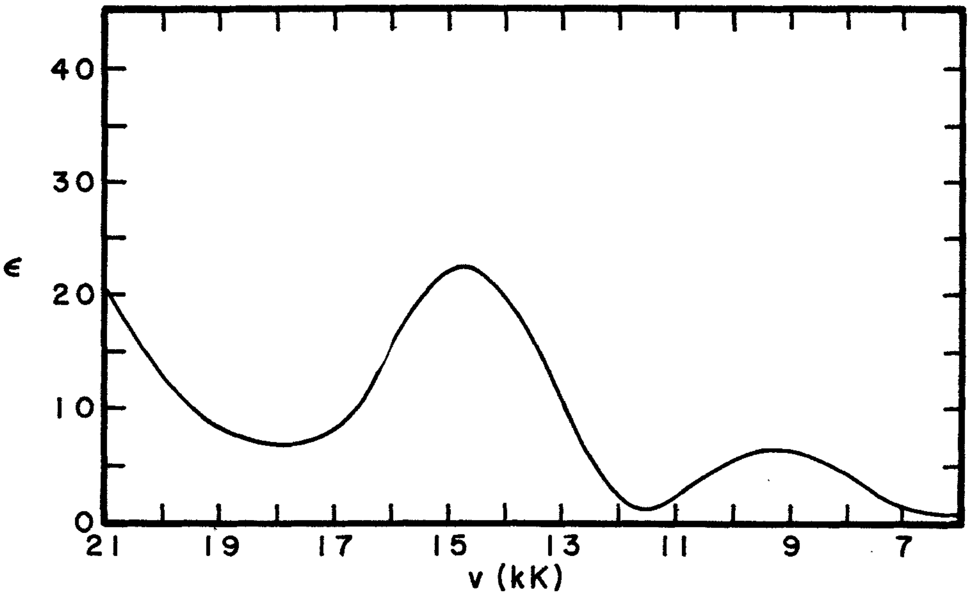


FIGURE 2
Electronic spectrum of $Ni(Cyhx\text{-}dtp)_2$ in neat n-propylamine.

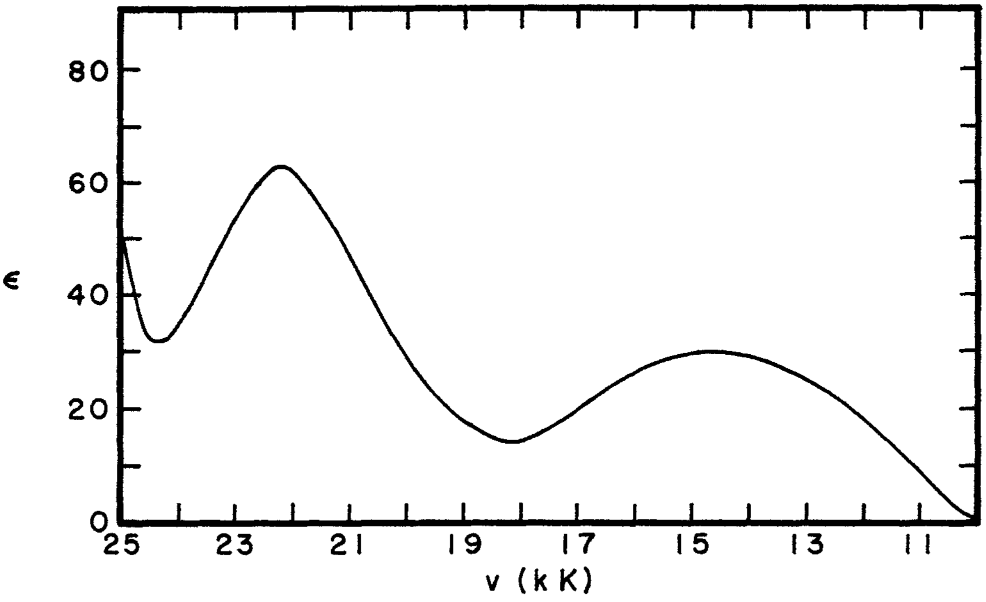
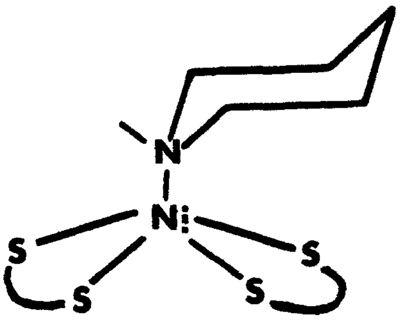


FIGURE 3
Electronic spectrum of $Ni(Cyhx\text{-}dtp)_2$ in neat piperidine.

ligand in good agreement with other reports.[27, 29, 30] In the present work tetragonal splitting[33] of the first electronic absorption band was not observed. This, coupled with the broadness of the first band, probably accounts for the anomalously high value of Dq for Cyhx-dtp. It is noted, however, that the octahedral model gives a good account of the observed spectra. For example, using $Dq = 922\ cm^{-1}$ and $\beta = 720\ cm^{-1}$, the spectrum of the isopropylamine adduct was calculated[34] to have bands at 9220, 14,698 and $23,762\ cm^{-1}$. Bands were observed at 9220, 14,700, and $23,810\ cm^{-1}$.

The electronic spectrum of $Ni(Cyhx\text{-}dtp)_2$ in neat piperidine is given in Figure 3. As expected for a secondary amine[27, 29] the observed spectrum is consistent with a five-coordinate geometry[35] for the adduct formed in solution. The appearance of the spectrum is suggestive of a distorted square pyramidal structure, I, for the adduct. Molecular models indicate that this form would be preferred compared to the trigonal bipyramidal structure.



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Furlani[35] has also noted that a high-spin bipyramid with sulfur ligands would be unusual. The extent of out-of-plane distortion of the dithiophosphate ligands cannot be assessed from available data. The only structural study of a five-coordinate nickel dithiophosphate complex is that for 2,9-dimethyl-1,10-phenanthrolinebis-(O,O′-dimethyldithiophosphato)nickel(II) which was found[36] to contain the highly distorted NiS_3N_2 chromophore. However, the high-spin quinoline adduct of the related bis(diethyldithiophosphinato)-nickel(II) complex has been shown[36] to contain five-coordinate nickel. Four sulfur atoms form the base of the pyramid and the apex is occupied by the nitrogen atom of quinoline. The four sulfur atoms lie in approximately one plane and nickel is 0.52 Å above the best plane passing through the sulfur atoms. In the absence of relevant structural and additional spectral data the existence of five-coordinate adducts of $Ni(Cyhx\text{-}dtp)_2$ with secondary amines with *possible* distorted square pyramidal geometry is all that can be concluded. Recently, Carlin and Losee[28] have examined several amine adducts of bis-(O,O′-diethyldithiophosphate)nickel(II). They report that the five-coordinate adducts with 2-picoline and 2,6-lutidine are diamagnetic but the diethylamine and di-n-butylamine adducts are paramagnetic. The formation constants for the amine mono-adducts of bis(O,O′-diethyldithiophosphato)-nickel(II) are small.[28] It is possible that Carlin and Losee's solutions in deuterochloroform did not contain a sufficient amount of the mono-adduct to give rise to observable nmr contact shifts. The 2-picoline mono-adduct of bis(O,O′-diisopropyldithiophosphato)nickel(II) exhibits[1] nmr shifts at room temperature consistent with a triplet ground state for the adduct complex. At least fifty five-coordinate amine adducts of nickel(II) dithiophosphates have been investigated in the authors' laboratory and all shown to possess triplet ground states.

In Table I it is seen that the electronic absorption bands of the adducts formed with secondary amines generally have larger molar absorptivities and transition oscillator strengths than the bands of *trans*-octahedral counterparts. This is in keeping with the presence of lower symmetry components in ligand fields in five-coordinate complexes. The N-methylpiperidine adduct was not sufficiently soluble in the amine to permit accurate determination of the molar absorption coefficients.

Generally, the green *trans*-octahedral adducts may be isolated in crystalline form by evaporating the solvent from solutions of nickel dithiophosphate chelates in neat amines. The stability of the adducts toward laboratory conditions is apparently a function of the volatility of the amines—the more volatile the amine, the less stable the adduct. Similar attempts to isolate solid five-coordinate adducts from solutions of nickel dithiophosphates in amines have been without success. The dark brown solids so obtained very readily lose amine to yield the purple starting material. Attempts to isolate relatively stable five-coordinate adducts would be more likely to be successful if large sterically crowded heterocyclic amines, e.g. quinoline, were employed. The instability of the five-coordinate adducts is probably associated with the greater stability of the planar geometry of nickel dithiophosphates. Thermogravimetric and differential thermal analysis and differential scanning calorimetry studies[14] of green *cis*-octahedral bis(O,O′-dialkyldithiophosphato)2,2′-dipyridine-nickel(II) complexes have demonstrated that during the thermal decomposition of the complexes two endothermic (bond-breaking) and two exothermic processes occur. The second of these exothermic processes is believed to involve the rearrangement of chelate rings which had been in a five-coordinate geometry to the planar geometry.

PMR SPECTRA OF PARAMAGNETIC ADDUCTS

Assignments for the pmr spectra of ligands were taken from standard sources[37] or based on the work of Weitkamp and Korte[38] when a first-order analysis did not apply. Typical pmr spectral data are shown in Figures 4 and 5. In Figure 4 it is apparent that the –NH– proton signal of diethylamine complexed with $Ni(Cyhx\text{-}dtp)_2$ is

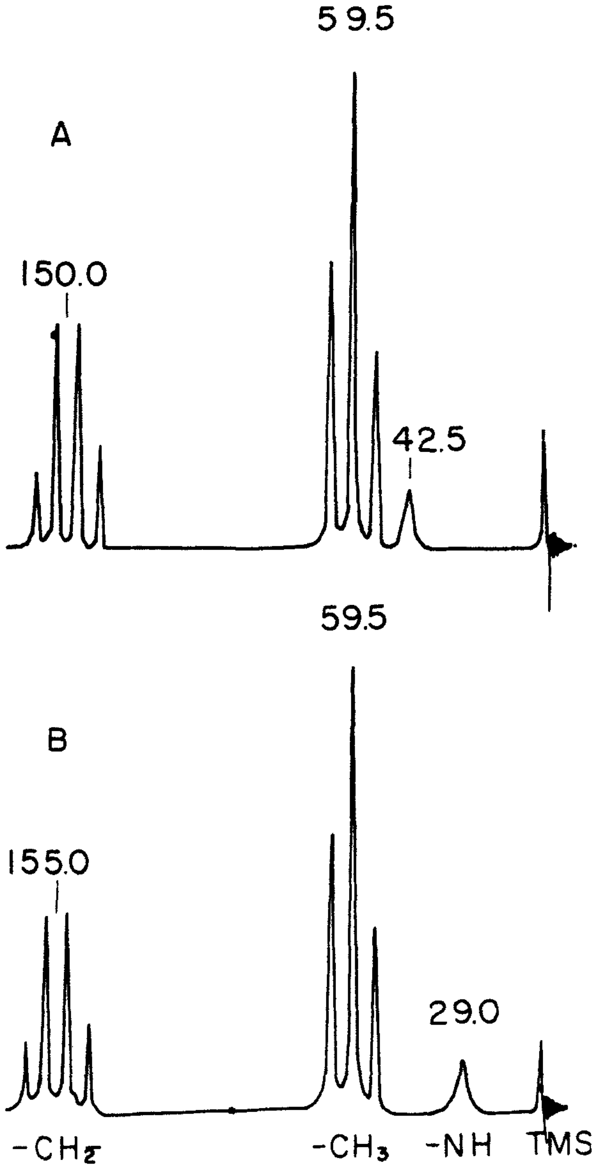

FIGURE 4 Pmr spectra of (A) diethylamine and (B) Ni(Cyhx-dtp)$_2$—13.7 × 10^{-3} M solution in diethylamine. Chemical shifts are in Hertz.

shifted upfield whereas the methylene absorption shifts downfield from TMS and the terminal CH_3-signal is unaffected. In Figure 5 the $-NH_2$ absorption of isopropylamine is shifted into the methyl absorption and then shifted further upfield upon addition of more nickel(II) complex. Amines which coordinate to nickel *via* nitrogen generally experience upfield shifts of –NH– or $-NH_2$ proton absorption. Although Ni(Cyhx–dtp)$_2$ cannot be considered a "shift reagent" in the usual sense,[39] the data suggest it can be used to aid in the assignment of pmr spectra of amines. The concentration dependence of the observed shifts in the pmr spectra of amines upon complexation with Ni(Cyhx–dtp)$_2$ is illustrated in Figures 6 and 7. Similar linear concentration dependencies were observed for all amine spectra. The attenuation of contact shifting with increasing distance from the metal ion as particularly noticeable in the chemical shift *versus*

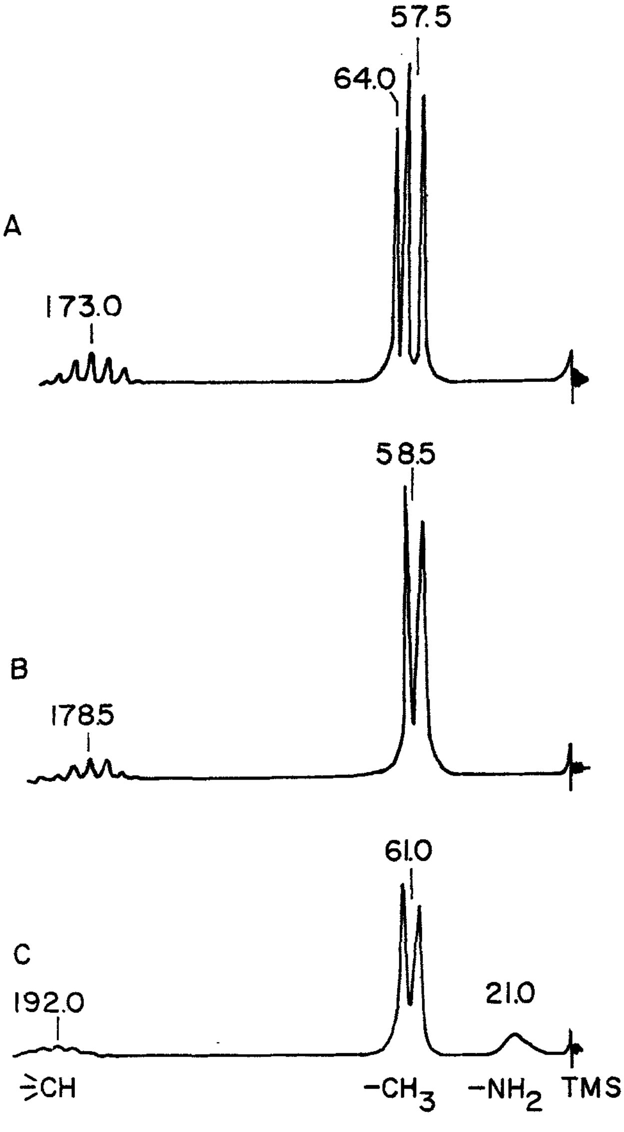

FIGURE 5 Pmr spectra of (A) isopropylamine, (B) Ni(Cyhx-dtp)$_2$—3.42 × 10^{-3} M solution and (C) Ni(Cyhx-dtp)$_2$—16.1 × 10^{-3}M solution in isopropylamine. Chemical shifts are in Hertz.

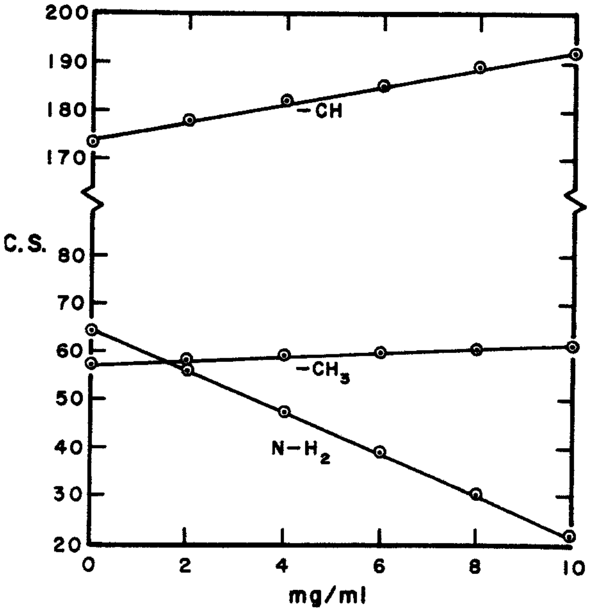

FIGURE 6 Chemical shifts (C.S.) in Hz from TMS *versus* concentration of Ni(Cyhx-dtp)$_2$ in diethylamine. Temperature = 35°.

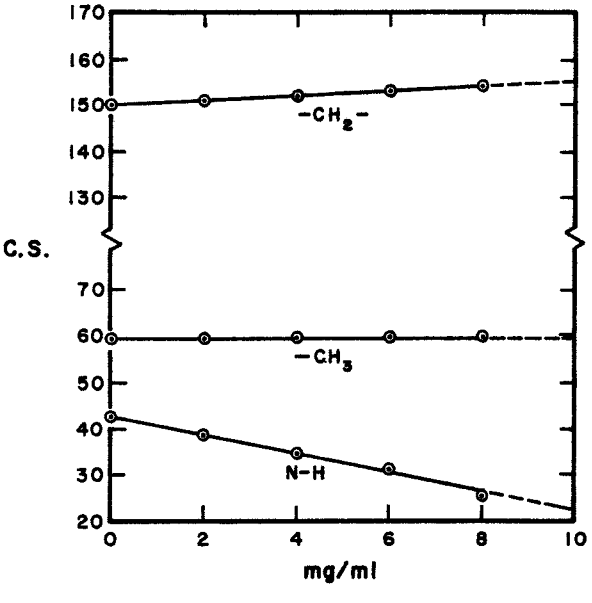

FIGURE 7 Chemical shifts (C.S.) in Hz from TMS *versus* concentration of Ni(Cyhx-dtp)$_2$ in isopropylamine. Temperature = 35°.

concentration plots. The chemical shift, electron spin-nuclear spin coupling constants and other parameters are summarized in Table II. The pKa's given in Table II were obtained from Reference 40.

The calculation of isotropic electron spin-nuclear spin hyperfine coupling constants, A_i, by the Bloembergen equation[13] involves the average g-value, g, of a paramagnetic system obeying the Curie law. The variation of A_i with g for contact shifts less than about 3000 Hz is on the order of a few thousandths of a gauss. Inspection of tabulated g-values[41] for nickel(II) compounds shows that they range from 2.05 to 2.38 with a value of about 2.2 being most frequently observed. Octahedral nickel(II) complexes possess a $^3A_{2g}$ ground state, the g-tensor should be isotropic and pseudo-contact or dipolar interaction should not be significant. The observed magnetic resonance shifts are then contact shifts related to the spin density on the nuclei. For complexes with approximate cubic symmetry the g-tensor would also be expected to be effectively isotropic. Anisotropy in g is rarely detected even in compounds of low symmetry.

The isotropic g-value for an octahedral nickel complex is given by[42]

$$g = 2.0023 - 8\lambda/10\,\mathrm{Dq}$$

where Dq is the ligand field splitting parameter and λ is the effective spin-orbit coupling constant ($\lambda = -322\,\mathrm{cm}^{-1}$ for the free ion). For $\mathrm{Ni(NH_3)_6}^{2+}$ and $\mathrm{Ni(H_2O)_6}^{2+}$ λ is found to be -216 and $-269\,\mathrm{cm}^{-1}$, respectively. With $\mathrm{Dq} = 950\,\mathrm{cm}^{-1}$ a value typical of *trans*-octahedral adducts of Ni(Cyhx-dtp)$_2$ and other sulfur complexes, corresponding g-values of 2.27 and 2.22 are obtained which are in good agreement with the values obtained from susceptibility determinations. Accurately determined g-values are rarely used in the calculation of A_i. In many instances the g-values cannot be measured since Ni(II) rapid spin-lattice relaxation times preclude solution measurements by electron spin resonance. The calculation of g in the usual manner, i.e. $\mu_{eff}/\sqrt{S(S+1)}$, is not without difficulties. Errors in μ_{eff} can arise from Pascal susceptibility corrections and the measurements themselves, e.g. the pmr method for susceptibility determination with chloroform as reference frequently yields anomalously high values of μ_{eff}, presumably because of various solvation and dissociation phenomena. In short, accurate g-values are only infrequently available for the calculation of electron spin-nuclear

TABLE II

Proton nuclear magnetic resonance parameters

Adduct	Group	δ, Ligand[a]	C.S., Hz[b]	Δν, Hz[c]	A_i[d], gauss
n-propylamine	N—CH_2—	2.47	−995	−846	+0.058
	—CH_2—	1.33	−365	−284	+0.020
pKa = 10.53	—CH_3	0.83	−58	0	—
	—NH_2	1.08	+3225	+3160	−0.218
isopropylamine	—CH—	2.88	−1160	−987	+0.068
pKa = 10.63	−CH_3	0.96	−338	−280	+0.019
	—NH_2	1.07	+2464	+2400	−0.165
2-phenylethylamine	aromatic	7.18	−431	0	—
	—CH_2—	2.53	−438	−286	+0.020
pKa = 9.83	—CH_2	2.61	−1567	−1410	+0.097
	—NH_2	0.96	+3018	+2960	−0.204
diethylamine	—CH_2—	2.50	−433	−283	+0.019
	CH_3—	0.99	−60	0	—
pKa = 10.98	—NH—	0.71	+1173	+1130	−0.078
morpholine	O—CH_2—	3.33	−490	−290	+0.020
	N—CH_2—	2.56	−508	−354	+0.024
pKa = 8.36	—NH—	2.20	+1562	+1430	−0.098
pyrrolidine	C—CH_2—	1.50	−90	0	—
	N—CH_2—	2.54	−1283	−1130	+0.078
pKa = 11.27	—NH—	1.99	+543	+423	−0.029
piperidine	N—CH_2—	2.60	−473	−353	+0.024
	C—CH_2—	1.40	−438	−282	+0.019
pKa = 10.84	—NH—	1.70	+1494	+1410	−0.097
N-methyl-piperidine	N—CH_2—	1.36	∼−102	∼−20	∼+0.001
	N—CH_3	2.03	∼−404	∼−282	∼+0.019
pKa = 9.86	—CH_2—	1.15	∼−129	0	—
2-methyl-piperidine[e]	A	0.92	−55	0	—
	B	1.52	+339	+248	−0.017
	C	2.74	−243	−79	+0.005
pKa 10.79	D	1.37	−110	−28	+0.002
3-methylpiperidine[f]	A	0.76	−46	0	—
	B	1.66	+1700	+1600	−0.110
pKa = 10.79	C	1.48	−89	0	—
	D	2.11	−431	−305	+0.021
	E	2.41	−399	−254	+0.017
	F	2.77	−531	−355	+0.024
4-methyl-piperidine[g]	A	0.85	−51	0	—
	B	1.64	+1648	+1550	−0.107
pKa = 10.78	C	1.32	−393	−310	+0.021
	D	2.41	−353	−209	+0.014
	E	2.92	−496	−321	+0.022

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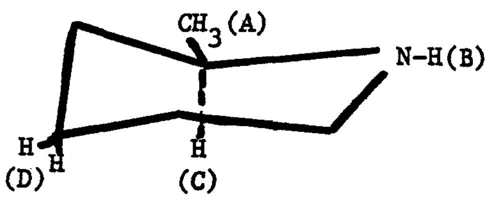
[a] Chemical shifts for free ligand relative to TMS. Temperature = 35°.

[b] Molar chemical shifts for complexes: C.S. = $C.S._{ligand} + \Delta\nu$. A positive sign indicates an upfield shift from TMS.

[c] Molar contact shifts for complexes relative to free ligand.

[d] Electron spin-nuclear spin hyperfine coupling constants calculated from the Bloembergen equation using g = 2.25.



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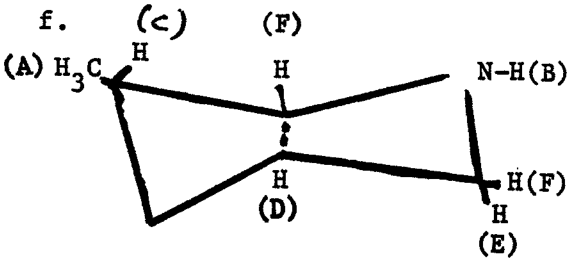
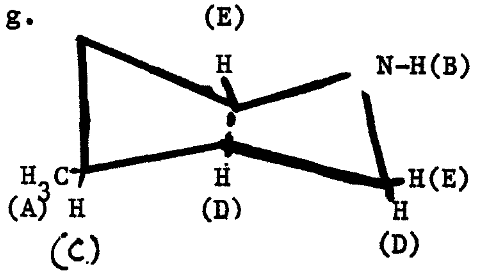


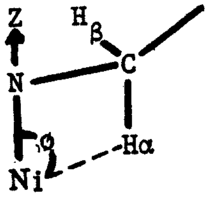
g.



spin hyperfine coupling constants. Since contact shifts are frequently less than 4000 Hz, we recommend the use of an average g-value of 2.25 for the calculation of A_i for octahedral nickel(II) complexes. Susceptibility data[35, 36] also suggests this value is suitable for five-coordinate adducts. The A_i listed in Table II have been calculated with $g = 2.25$.

In Table II negative spin densities are found for all NH protons. The basicity of the nitrogen atom co-ordinated to nickel does not correlate with the magnitude of the upfield NH proton contact shift. Primary amines, which form octahedral adducts with Ni(Cyhx–dtp)$_2$, exhibit large NH contact shifts on the order of 3000 Hz whereas secondary amines, which form five-coordinate adducts, have NH contact shifts on the order of 1400 Hz. If the number[18] of amines coordinated to nickel is taken into account, i.e. divide the contact shifts for the primary amine diadducts by 2 in order to obtain the shift per amine molecule, the shift differences between primary and secondary amines vanish. This suggests that in favorable instances it should be possible to determine the coordination number of nickel(II) in amine solutions from a determination of ν_c for the amine protons. NMR and electronic spectra and conductometric data are being obtained for solutions of anhydrous metal halides in amines to further explore this result of the present study.

Apparently, steric factors contribute significantly to the observed NH and CH contact shifts. Steric crowding undoubtedly accounts for the five-coordinate geometry of adducts of Ni(Cyhx-dtp)$_2$ with secondary amines and is associated with the lack of correlation of NH contact shifts with ligand basicity. Metal–ligand atom separations are expected to generally dominate the contact shift behavior of octahedral nickel complexes. Pratt[7, 8] and Reilley[43] and their co-workers have shown that the contact shifts of CH$_2$ and CH protons in aminoacid and substituted acetate complexes are very dependent on ligand conformation. In the fragment,



the contact shifts for Hα and Hβ depend[43] on the dihedral angle, ϕ, between Ni and H. The methyl groups of the carbon-substituted methyl piperidines are remarkably unaffected by coordination of the amines to nickel whereas the CH$_2$ protons even two bonds away from nitrogen are shifted downfield. In contrast, the CH$_3$ protons in N-methylpiperidine are strongly shifted downfield. Unfortunately, the low solubility of the N-methylpiperidine adduct precluded accurate evaluation of the contact shifts. However, the estimated shifts and A_i in Table II are expected to be within 25% of the true values. Roughly comparable behavior is exhibited by the methyl protons in the adducts of Ni(Cyhx-dtp)$_2$ with propylamines. This Ni–H distance dependence, which is not[4] likely to arise from dipolar contributions to the observed pmr shifts implies that the σ-delocalization mechanism invoked to account for the downfield shift of protons bound to carbon must include consideration of direct metal-proton interactions. Fitzgerald and Drago[5] employed extended Huckel molecular orbital calculations involving only the ligand to account for contact shifts of carbon bound protons in alkylaminenickel(II) complexes. The present work indicates that when the barriers between ligand conformations exceed rotational barriers the process of taking numerical averages over conformations[5] is inadequate to account for observed spectra.

In their work on the piperidine adducts of nickel(II) and cobalt(II) acetylacetonate Happe and Ward[16] did not observe contact shifts for the proton bound to nitrogen. This was a consequence of working with dilute solutions of the amine and the severe line broadening of the amine proton resonance absorption by the paramagnetic complexes. Recent INDO molecular orbital calculations by Scarlett *et al.*[45] for a variety of ligands have affirmed that the contact shifts in nickel(II) complexes arise from the transfer of negative spin density from the ligand to the metal and also predicted negative spin density on the amine proton of piperidine upon complexation with nickel. The present work confirms this prediction and suggests the INDO calculations may be generally useful for describing the contact shifts of amine complexes.

SUMMARY

The pmr and electronic spectra of eleven adducts of Ni(Cyhx–dtp)$_2$ have been determined. Secondary amines form five-coordinate adducts with approximate C_{4v} symmetry and primary amines give *trans*-octahedral diadducts. The NH pmr contact shifts, corresponding to negative spin densities arising from σ-spin polarization, do not correlate with the basicity of the amine since steric effects dominate the contact shift behavior of NH and CH protons. From a consideration of susceptibility measurements and tabulated g-values for nickel(II) complexes a value of $g = 2.25$ is recommended for the calculation of electron spin-nuclear spin hyperfine coupling constants in high-spin five-coordinate and six-coordinate nickel(II) complexes with undetermined g-values.

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REFERENCES

1. Part IV. H. E. Francis, G. L. Tincher, W. F. Wagner, J. R. Wasson, and G. M. Woltermann, *Inorg. Chem.* **10** (1971), in press.
2. E. W. Randall and D. Shaw, *J. Chem. Soc.* (A), 2867 (1969). These authors recommend referring to chemical shifts caused by paramagnetic agencies as Knight shifts (a term originally applied to metals). This generalized use of the term "Knight shift" has the advantage that it does not imply a particular shift mechanism as do the terms "contact" and "dipolar" or "pseudo-contact" shift.
3. (a) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965). (b) E. de Boer and H. van Willigen, *Progr. Nucl. Magn. Res. Spectry*, **2**, 111 (1967). (c) P. J. McCarthy in "Spectroscopy and structure of metal chelate compounds", K. Nakamoto and P. J. McCarthy, Eds., J. Wiley and Sons, Inc., New York, 1968, Ch. 6. (d) R. H. Holm, *Accts. Chem. Res.* **2**, 307 (1969).
4. B. B. Wayland and W. L. Rice, *J. Chem. Phys.* **45**, 3150 (1966); *Inorg. Chem.*, **6**, 2270 (1967).
5. (a) R. J. Fitzgerald and R. S. Drago, *J. Am. Chem. Soc.* **89**, 2879 (1967). (b) R. J. Fitzgerald and R. S. Drago, *ibid.* **90**, 2523 (1968). (c) R. J. Fitzgerald, Ph.D. thesis, University of Illinois, 1968.
6. T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Am. Chem. Soc.* **92**, 1267 (1970).
7. R. S. Milner and L. Pratt, *Disc. Faraday Soc.* **34**, 88 (1962).
8 L. Pratt and B. B. Smith, *Trans. Faraday Soc.* **65**, 915 (1969).
9. R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.* **6**, 430 (1967).
10. D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Am. Chem. Soc.*, **89**, 4040 (1967).
11. J. P. M. Bailey and R. M. Golding, *Mol. Phys.* **12**, 49 (1967).
12. M. C. R. Symons, *Tetrahedron*, **18**, 333 (1962); J. P. Colpa and E. de Boer, *Mol. Phys.* **7**, 333 (1964); D. H. Levy, *Mol. Phys.* **10**, 233 (1966).
13. J. I. Zink and R. S. Drago, *J. Amer. Chem. Soc.* **92**, 5339 (1970).
14. G. M. Woltermann, W. R. Vincent, C. Cabrera, and J. R. Wasson, to be submitted; J. R. Wasson, G. L. Tincher, H. E. Francis, J. R. Angus, and W. F. Wagner, to be submitted.
15. J. R. Angus, G. M. Woltermann, W. R. Vincent, and J. R. Wasson, *J. Inorg. Nucl. Chem.* **33**, (1971), in press.
16. J. Happe and R. L. Ward, *J. Chem. Phys.* **39**, 1211 (1963).
17. T. W. Mastin, G. R. Norman, and E. A. Weilmuenster, *J. Amer. Chem. Soc.* **67**, 1662 (1945).
18. N. Bloembergen, *J. Chem. Phys.* **27**, 595 (1957).
19. D. F. Evans, *J. Chem. Soc.* 2003 (1959); J. L. Deutsch and S. M. Poling, *J. Chem. Educ.* **46**, 167 (1969).
20. G. M. Woltermann and J. R. Wasson, *Inorg. Nucl. Chem. Letters* **6**, 475 (1970).
21. D. M. Adams, "Metal-ligand and related vibrations" Edward Arnold Publishers Ltd., London, 1967.
22. K. Shobatake, University of Chicago, Private communications.
23. C. Frenzel, G. M. Woltermann, W. R. Vincent, and J. R. Wasson, unpublished results.
24. D. J. MacDonald, *Inorg. Chem.* **6**, 2269 (1969) and references therein.

25. H. B. Gray, *Transition Metal Chem.* **1**, 240 (1965); S. I. Supack, E. Bilig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.* **86**, 4594 (1964); A. R. Latham, V. C. Hascall, and H. B. Gray, *Inorg. Chem.* **7**, 788 (1965).
26. C. K. Jorgensen, *J. Inorg. Nucl. Chem.* **24**, 1571 (1962); *Acta Chem. Scand.* **17**, 553 (1963).
27. R. L. Carlin, J. S. Dubnoff, and W. T. Huntress, *Proc, Chem. Soc.* 228 (1964); R. L. Carlin and D. B. Losee. *Inorg. Chem.* **9**, 2087 (1970).
28. J. R. Angus, G. M. Woltermann, and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **33** (1971), in press.
29. A. Sgamellotti, C. Furlani, and F. Magrini, *ibid.* **30**, 2655 (1968).
30. A. Sgamellotti, P. Porta, and E. Cervone, *Ric. Sci.* **38**, 1223 (1968).
31. D. Coucouvanis and J. P. Fackler, Jr., *Inorg. Chem.* **6**, 2047 (1967).
32. R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *ibid.* **2**, 1056 (1963).
33. A. B. P. Lever, *Coord. Chem. Revs.*, **3**, 119 (1968), and references therein.
34. J. R. Wasson, *J. Chem. Educ.* **47**, 371 (1970).
35. C. Furlani, *Coord. Chem. Revs.*, **3**, 141 (1968); M. Campolini, *Structure and Bonding*, **6**, 52 (1969); M. Campolini and J. Gelsomini, *Inorg. Chem.* **6**, 1821 (1967).
36. P. S. Shetty, R. E. Ballard, and Q. Fernando, *Chem. Commun.* 717 (1969); P. S. Shetty and Q. Fernando, *J. Amer. Chem. Soc.* **92**, 3964 (1970).
37. "High resolution NMR spectra catalog", Varian Associates, Palo Alto, California, 1963; "High resolution NMR spectra", Sadtler Research Laborataries, Inc., Philadelphia, Pennsylvania, 1967.
38. H. Weitkemp and F. Korte, *Chem. Ber.* **95**, 2896 (1962); J. C. N. Ma and E. W. Warnhoff, *Can. J. Chem.* **43**, 1849 (1965).
39. C. C. Hinckley, *J. Amer. Chem. Soc.* **91**, 5160 (1969); J. K. M. Sanders and D. H. Williams, *Chem. Commun.* 422 (1970); J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *ibid.* 749 (1970).
40. Y. Yukawa, ed., "Handbook of organic structural analysis", W. A. Benjamin, Inc., New York, 1965, pp. 584–613; J. F. King in "Elucidation of structures by physical and chemical methods', K. W. Bentlye, ed., Interscience Publishers, New York, 1963, Part I, Ch. 6; piperidines—J. Lakomy, A. Silhankova, M. Ferles, and O. Exner, *Coll. Czech. Chem. Comm.* **33**, 1700 (1968).
41. B. R. McGarvey, *Transitional Metal Chemistry*, **3**, 89 (1966); H. A. Kuska and M. T. Rogers in "Radical ions", E. T. Kaiser and L. Kevans, eds., Interscience Publishers, New York, 1968, p. 579.
42. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970, p. 450.
43. F. F.-L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *ibid.* **9**, 1139 (1970); L. E. Erickson, F. F.-L. Ho, and C. N. Reilley, *ibid.* **9**, 1148 (1970), and references therein.
44. R. J. Kurland and B. R. McGarvey, *J. Magn. Res.* **2**, 286 (1970).
45. M. J. Scarlett, A. T. Casey, and R. A. Craig, *Aust. J. Chem.* **23**, 1333 (1970).