Synthesis and Characterisation of the Reaction Products from Bis-(thiosalicylohydrazidato)nickel(II) in Base and Acid Solution

By **Prasanta K. Biswas** and **Nirmalendu Ray Chaudhuri,*** Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

Bis(thiosalicylohydrazidato)nickel(II), $[Ni(HL)_2]$ (1) transforms to [NiLL'] on reacting with nucleophiles (L') in the presence of ethanolic K[OH], where H_2L = thiosalicylohydrazide, *o*-$HOC_6H_4C(=S)N^aHN^bH_2$, and L' = H_2O, NEt_3, pyridine, 2-methylpyridine, 2,6-dimethylpyridine, 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), propane-1,3-diamine, or *NN'*-diethylethylenediamine. But, in contrast, with ethylenediamine (en), complex (1) transforms to $[Ni_2L_2(en)]$ where en bridges two metal ions through the terminal nitrogen atoms. In [NiLL'], thiosalicylohydrazide acts as a dibasic tridentate ligand and co-ordinates through (O,N^bS) sites. Complex (1) reacts with acetone to form bis(acetone thiosalicylhydrazonato)nickel(II) and also forms an adduct with dimethyl sulphoxide in acidic medium. In both these cases the bonding sites (N^a,O) observed in the parent species (1) change to (S,N^b) on reaction. In $[Ni(H_2L)_2]Cl_2\cdot 5H_2O$ and $[Ni(H_2L)_2][HSO_4]_2\cdot 2H_2O$ however, formed by treatment of (1) with mineral acid, no alteration of the bonding sites takes place. All the complexes, except [NiL(bipy)] and [NiL(phen)] which possess high-spin five-co-ordinate geometry, are square planar. All the reaction products are characterised by elemental analyses, magnetic moments, conductance, and spectral (^1H n.m.r., i.r., far-i.r., and electronic) data.

EXTENSIVE studies on the complexation of various thiohydrazides with transition-metal ions are few [1-3] due to the rapid cyclisation and decomposition of the ligands.[4] Recently, we have reported [5] the novel ligational behaviour of thiosalicylohydrazide, *o*-$HOC_6H_4C(=S)N^aHN^bH_2$ (H_2L), and its complexes with cobalt(II), nickel(II), copper(II), and palladium(II) ions. Among these complexes, H_2L produces chelates of the type $[Ni(HL)_2]$ in alcoholic medium, showing monobasic bidentate character.

Investigations on ligational properties of thiohydrazides and their nickel(II) complexes in acidic as well as in alkaline medium have previously been of great interest.[1-3] Jensen and Miquel [1] prepared nickel complexes with thiobenzohydrazides in weak alkaline medium (ammonia). Larsen and co-workers [2,3] showed that a nickel(II) complex of thioacetohydrazide (Htah) disproportionated in presence of acid while the disproportionated compound produced one mole of ligand in the presence of alkali [equations (1) and (2)].

$$3\,[Ni(tah)_2] + 6\,H^+ \longrightarrow 2\,[Ni(Htah)_3]^{2+} + Ni^{2+} \quad (1)$$

$$[Ni(Htah)_3]^{2+} + 2\,OH^- \longrightarrow [Ni(tah)_2] + Htah + 2\,H_2O \quad (2)$$

Although the thiohydrazide unit ($-\overset{S}{\overset{\|}{C}}-N^aH-N^bH_2$) of H_2L in $[Ni(HL)_2]$ would predict it to follow the reactions (1) and (2), in the presence of excess nucleophiles (L') and ethanolic K[OH] it is probable that the reaction (3) may also occur, since the bonding sites of $[Ni(HL)_2]$,

$$[Ni(HL)_2] + OH^- + L' \longrightarrow [NiLL'] + H_2O + HL^- \quad (3)$$

unlike those of $[Ni(tah)_2]$, are (N^a,O) and the ligand (H_2L) possibly acts as dibasic tridentate in alkaline medium where the thiolo-form [equation (4)] is preferred, similar to the observation made by Livingstone and co-workers.[6]

$$-\overset{S}{\overset{\|}{C}}-N^aH-N^bH_2 + OH^- \longrightarrow -\overset{S^-}{\overset{|}{C}}=N^a-N^bH_2 + H_2O \quad (4)$$

On the other hand, it is likely that $[Ni(HL)_2]$ may react with acids to form acid salts [equation (5)] due to the presence of a free amino-group, instead of disproportionating.[2,3]

$$[Ni(HL)_2] + 2\,H^+ \longrightarrow [Ni(H_2L)_2]^{2+} \quad (5)$$

It is quite likely that $[Ni(HL)_2]$ can give rise to a condensation product by reaction with ketones, similar to Curtis [7] type condensation reactions as also shown by some thiohydrazides.[8-11]

For the reasons mentioned above it seemed interesting to investigate the reactions of $[Ni(HL)_2]$, with different types of nucleophiles in alkali, with ketones, and acids. This paper deals with the synthesis and characterisation of several mixed chelates, thiohydrazonate adducts, and acid salts derived from bis(thiosalicylohydrazidato)-nickel(II).

EXPERIMENTAL

All the chemicals used were A.R. grade and the solvents used for electronic spectra were distilled before use. Elemental analyses (C,H,N) were determined by the Microanalytical section of the Australian Mineral Development Laboratories as well as by the microanalytical laboratory of this Institute.

Infrared (KBr disc, 400—4 000 cm^{-1}), far-i.r. (Polythene disc, 100—400 cm^{-1}), and electronic spectra were recorded using Beckman IR 20A, Beckman IR-720M, and Cary 17D spectrophotometers respectively. Hydrogen-1 n.m.r. spectra ($SiMe_4$ as calibrant) were obtained using a Varian EM-390 90-MHz instrument. Magnetic susceptibilities were determined at room temperature by the Guoy technique using $Hg[Co(SCN)_4]$ as a standard; diamagnetic correction was made using literature data.[12] Conductivity data were obtained using a Philips conductivity meter.

Starting Materials.—Thiosalicylohydrazide (H_2L) was prepared following the method described by Jensen and Pederson [4] starting from carboxymethyl *o*-hydroxydithio-

benzoate. Bis(thiosalicylohydrazidato)nickel(II), $[Ni(HL)_2]$, was prepared by mixing an ethanolic solution of nickel(II) chloride (1 mmol) (dropwise and stirring) with an ethanolic solution of thiosalicylohydrazide (2 mmol).[5] It was recrystallised from dmf–H_2O and dried in a vacuum desiccator.

*Preparation of the Complexes.**—$[Ni^{II}L(py)]$. An ethanol solution (25 cm^3) of $[Ni(HL)_2]$ was added to a solution prepared by dissolving K[OH] (0.25 g) in ethanol (25 cm^3). The mixture was stirred for 30 min and then filtered. Pyridine (2 cm^3) was added to the filtrate and the mixture was stirred for 4 h. Deep brown crystals separated and these were washed thoroughly with water and dried in a vacuum desiccator.

$[Ni^{II}L(L')]$. These complexes were prepared similarly to that above [L′ = H_2O (recrystallised from acetone; washed with concentrated ammonia), NEt_3 (recrystallised from acetone), 2Me-py,† $2,6Me_2$-py,† bipy,† phen,† pd,† or deen (recrystallised from chloroform)].

$[Ni^{II}(HL{\cdot}acetone)_2]$. Acetone (10 cm^3) and $[Ni(HL)_2]$ (1 mmol) were mixed. Dilute perchloric acid (2 cm^3, 1 mol dm^{-3}) was added to the mixture. The mixture was stirred for 30 min and then filtered. The filtrate was kept overnight in a desiccator while fine brown crystals separated out. The crystals were collected, washed with water-ethanol mixture, dried in a vacuum desiccator, and recrystallised from chloroform.

$[Ni^{II}(HL)_2]{\cdot}2dmso$. Dilute sulphuric acid (2 cm^3, 0.5 mol dm^{-3}) was added to $[Ni(HL)_2]$ (1 mmol) dissolved in dmso (5 cm^3). The mixture was stirred for 30 min and then water was added until a turbidity appeared. The solution was kept overnight. Beautiful light pink crystals separated out. The crystals were collected and washed with water and dried in a vacuum desiccator.

$[Ni^{II}(H_2L)_2]X_2{\cdot}nH_2O$ (X = Cl^-, n = 5; X = HSO_4^-, n = 2). Hydrochloric (2 cm^3, 12 mol dm^{-3}) or sulphuric acid (2 cm^3, 6 mol dm^{-3}) was added to $[Ni(HL)_2]$ (1 mmol) suspended in water (10 cm^3) and stirred for 30 min. The pale yellow $[Ni(HL)_2]$ turned to a deep red solid. This compound was filtered off and washed initially by dilute (0.2 mol dm^{-3}) acid solution and finally by water and then dried in a vacuum desiccator using fused $CaCl_2$–K[OH] as desiccating agent.

* Abbreviations used: py = pyridine, dmf = dimethylformamide, 2Me-py = 2-methylpyridine, $2,6Me_2$-py = 2,6-dimethylpyridine, bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, pd = propane-1,3-diamine, deen = *NN*′-diethylethylenediamine, en = ethylenediamine, dmso = dimethyl sulphoxide, HL·acetone = acetone thiosalicylhydrazonate [o-$HOC_6H_4C(S^-)=N^a$–$N^b=CMe_2$].

† Recrystallisation was from dmso–H_2O and adhered dmso was removed from the crystals by washing with ethanol.

RESULTS AND DISCUSSION

Scheme 1 summarises the reactions studied. The analytical, magnetic moment, and conductance data, ^1H n.m.r., i.r., far-i.r., and electronic spectral data for the reaction products are given in Tables 1—4.

The assignments of pertinent bands (Table 3) in the i.r. spectra which are important for metal–ligand bond formation have been made from a comparison of the spectra of these complexes with those of thiosalicylohydrazide (H_2L), its derivatives, deuteriated derivatives, their metal complexes,[5] and metal complexes of thioacetohydrazide,[13] thioamides,[14,15] and thiocarbohydrazide.[16]

TABLE 1

Conductance, magnetic, and analytical data (calculated values in parentheses) of complexes derived from bis(thiosalicylohydrazidato)nickel(II)

Compound	Colour	Λ^a/Ω^{-1} cm^2 mol^{-1}	$\mu_{eff.}$/ B.M.	Analysis (%) C	H	N	Ni
$[NiL(OH_2)]$	Brown	7.1 [b]	[c]	34.4 (34.6)	3.2 (3.3)	11.7 (11.5)	24.2 (24.2)
$[NiL(NEt_3)]$	Red	3.2 [d]	[c]	47.3 (47.9)	6.5 (6.4)	12.9 (12.9)	18.1 (18.0)
[NiL(py)]	Brown	2.2 [d]	[c]	47.2 (47.4)	3.6 (3.6)	13.7 (13.8)	19.3 (19.3)
[NiL(2Me-py)]	Brown	1.6 [d]	[c]	49.5 (49.1)	4.1 (4.1)	13.4 (13.2)	18.5 (18.5)
$[NiL(2,6Me_2\text{-py})]$	Brown	1.0 [d]	[c]	50.3 (50.6)	4.6 (4.5)	12.6 (12.7)	17.7 (17.7)
[NiL(bipy)]	Brown	2.5 [d]	3.05	54.9 (53.6)	3.7 (3.7)	14.8 (14.7)	15.4 (15.4)
[NiL(phen)]	Brown	2.2 [d]	3.10	57.0 (56.3)	3.5 (3.4)	13.9 (13.8)	14.5 (14.5)
$[Ni_2L_2(en)]$	Red	1.6 [d]	[c]	37.6 (37.7)	4.0 (3.9)	16.5 (16.5)	23.1 (23.0)
[NiL(pd)]	Red	1.2 [d]	[c]	40.5 (40.2)	5.4 (5.3)	18.8 (18.7)	19.7 (19.6)
[NiL(deen)]	Red	1.0 [b]	[c]	45.2 (45.8)	6.4 (6.4)	16.5 (16.4)	17.2 (17.2)
$[Ni(HL{\cdot}acetone)_2]$	Brown	0.3 [b]	[c]	50.7 (50.8)	4.7 (4.6)	11.9 (11.8)	12.5 (12.4)
$[Ni(HL)_2]{\cdot}2dmso$	Pink	3.5 [d]	[c]	39.4 (39.4)	4.6 (4.7)	10.3 (10.2)	10.7 (10.7)
$[Ni(H_2L)_2]Cl_2{\cdot}5H_2O$	Red	65.7 [d]	[c]	30.3 (30.2)	4.8 (4.7)	10.2 (10.1)	10.6 (10.5)
$[Ni(H_2L)_2][HSO_4]_2{\cdot}2H_2O$	Red	72.3 [d]	[c]	26.9 (26.9)	3.5 (3.5)	8.8 (9.0)	9.4 (9.4)

[a] Solutions *ca.* 10^{-3} mol dm^{-3}. [b] In acetone. [c] Diamagnetic. [d] In dimethylformamide.

Reaction of Unidentate Nucleophiles with Bis(thiosalicylohydrazidato)nickel(II), $[Ni(HL)_2]$ (1).—The pale yellow complex turns deep red in the presence of ethanolic K[OH] and slowly goes into solution, which on treatment with a nucleophile (L′) followed by stirring gives either deep brown or red crystals of the neutral chelate [NiLL′] (3), where L′ = NEt_3, py, 2Me-py or $2,6Me_2$-py. The loss of two acidic protons from H_2L is well identified by the ^1H n.m.r. signals (Table 2) of a few complexes of the [NiLL′] type. The involvement of (O,N^b,S) sites of H_2L in bonding is well understood by the absence of ν(OH) at *ca.* 3 500 cm^{-1}, a negative shift of $\beta(NH_2)$, either weakening or disappearing of $\rho_w(NH_2)$, and the presence of bands due to $=\overset{|}{C}-S^-$ as observed in H_2L which exists as the zwitter ion,[5] o-$HOC_6H_4C(S^-)=N^a$–$N^bH_3^+$. The presence of sharp bands at *ca.* 2 900 cm^{-1} in $[NiL(NEt_3)]$ is due to ν(CH) which supports the existence of NEt_3 in the complex. The Ni-N (NEt_3) bonding is inferred from the presence of downfield shifts of 0.20 and 0.60 p.p.m. for the methyl and methylene signals respectively compared with those of free NEt_3.[17] The presence of py in [NiL(py)] is confirmed [18] by the in-plane and out-of-plane

TABLE 2

Hydrogen-1 n.m.r. spectral data (δ/p.p.m.) [a] of complexes derived from bis(thiosalicylohydrazidato)nickel(II)

Compound	Ring protons	Methyl protons	Methylene protons	Protons bound to nitrogen	*ortho*-Hydroxy proton
H_2L [b]	7.10m (3) 8.30d (1)			3.50s,br (2) [c,d] 10.65s,br (1) [d,e]	11.23s,br (1) [d]
$[Ni(HL)_2]$ [f]	7.00m, 7.30m } (6) 8.60d (2)			7.90—10.66br (4) [c,d] 11.16—13.16br (2) [d,e] 2.35s (2) [c,d]	
$[NiL(OH_2)]$ [b,g]	6.90m (3) 8.35d (1)				
$[NiL(NEt_3)]$ [b]	7.00m (3) 8.35d (1)	1.15t (9)	3.02m (6)	3.80s,br (2) [c,d]	
$[NiL(2,6Me_2\text{-py})]$ [f]	7.00d, 7.30s, 7.50m } (7)	2.55s (6)		4.90s (2) [c,d]	
[NiL(deen)] [h]	6.90m (3) 8.30d (1)	1.00t (6)	2.50m (8)	2.00s,br (2) [c,d] 1.60m (2) [d]	
deen [h]		1.00t (6)	2.44m (8)	1.30s (2) [d]	
$[Ni(HL\cdot acetone)_2]$ [h]	7.00m (6) 8.20d (2)	2.40s (6) 2.80s (6)			11.66s,br (2) [d]
$[Ni(HL)_2]\cdot 2dmso$ [f]	7.27m(6) 8.60d (2)	2.50s (12)		9.40s,br (4) [c,d]	13.00s,br (2) [d]

[a] Relative to $SiMe_4$, solvent as stated; s = singlet, d = doublet, m = multiplet, br = broad. [b] In $[^2H_6]$dmso solution. [c] Protons bound to N^b nitrogen of H_2L. [d] Signal disappears on shaking with D_2O. [e] Proton bound to N^a nitrogen of H_2L. [f] In $[^2H_5]$-pyridine solution. [g] Signal for H_2O appears at 3.15 p.p.m. as a singlet. [h] In $CDCl_3$ solution.

ring deformations of py at 645 and 440 cm^{-1} respectively. The medium intensity bands at 223, 235, and 270 cm^{-1} are probably due to the ν(M-N) where N belongs to pyridine,[18] 2-methylpyridine,[19] and 2,6-dimethylpyridine[20] of [NiL(py)], [NiL(2Me-py)], and $[NiL(2,6Me_2\text{-py})]$ respectively. The signal at δ 2.55 p.p.m. for the two methyls of $2,6Me_2$-py in $[NiL(2,6Me_2\text{-py})]$ confirms the presence of the pyridine derivative as is evident from the ^1H n.m.r. spectrum [21] of 2,6-dimethylpyridine in $CDCl_3$.

These four compounds are diamagnetic and appreciably soluble in polar solvents and the almost identical electronic spectra in polar solvents (Table 4) show no

TABLE 3

Infrared and far-i.r. spectral data [a] (cm^{-1}) of complexes derived from bis(thiosalicylohydrazidato)nickel(II)

Compound	ν(OH)	ν(NH_2)	β(NH_2)/(NH) + ν(CN)	$\rho_w(NH_2)$	ν(CS) + ν(NH) + ν(CN)	ν(MN) + ν(MO) + ν(MS)	ν(MN) (N of L')
H_2L	3 520w,br	3 240s, 2 880—2 720m,br [b]	1 462s	935s	760s, 740vs		
$[Ni(HL)_2]$		3 200s	1 482vs, 1 445m	935w	750s	412s, 292s	
$[NiL(OH_2)]$ [c]	3 340m, 3 310m, 3 240m	3 160w, 3 000w	1 485vs	930vw	760m, 750 (sh), 740s	435w,br, 385w, 325m	
$[NiL(NEt_3)]$		3 220s, 3 050m	1 480vs	935vw	752vs	390m, 350w, 295 (sh)	
[NiL(py)] [d]		3 100 (sh), 3 050m	1 485vs	930w	760 (sh), 740vs	440s,[e] 414w, 364w, 315m	223m
[NiL(2Me-py)]		3 060m	1 488vs	935vw	765 (sh), 752s	420w, 380m, 300w	235m
$[NiL(2,6Me_2\text{-py})]$		3 045m	1 485vs		780s, 740s	437s, 391s, 364s 303m	276m
[NiL(bipy)]		3 060m	1 475vs, 1 445vs [f]		765vs,[f] 735vs	413vs, 376m, 345vs	290vs, 274m, 250m
[NiL(phen)]		3 050m	1 475vs		847s,[g] 760s, 730vs [g]	410w, 380s, 345m	295s, 270w, 242s
$[Ni_2L_2(en)]$		3 250m, 3 130w, 3 060w	1 490vs, 1 465s		762s, 752 (sh), 730w	418w, 388 (sh), 338vs	396m, 285m
[NiL(pd)]		3 350w, 3 290m, 3 270m, 3 020m	1 480vs, 1 455s	930m	755vs, 720w	420w, 370 (sh), 320m	340 (sh)
[NiL(deen)]		3 180m, 3 095vs	1 470vs,		740vs, 710w	440m, 378m, 306w	392, 282s, 267m
$[Ni(HL\cdot acetone)_2]$	3 500w,br		1 480vs [h]		755vs, 730 (sh)	422m, 405s, 356m	
$[Ni(HL)_2]\cdot 2dmso$ [i]	3 420m,br	3 220w, 3 060m	1 495vs		762s, 745m	440 (sh), 390m, 330m	
$[Ni(H_2L)_2]Cl_2\cdot 5H_2O$ [j]	3 560 (sh), 3 330s,br	3 100—2700s,br [b]	1 485m		745vs, 735 (sh)	415m,br, 320 (sh)	
$[Ni(H_2L)_2][HSO_4]_2\cdot 2H_2O$ [k]	3 400s,br	3 100—2 800s,br [b]	1 450s		750m, 735m	450m,br, 350m,br	

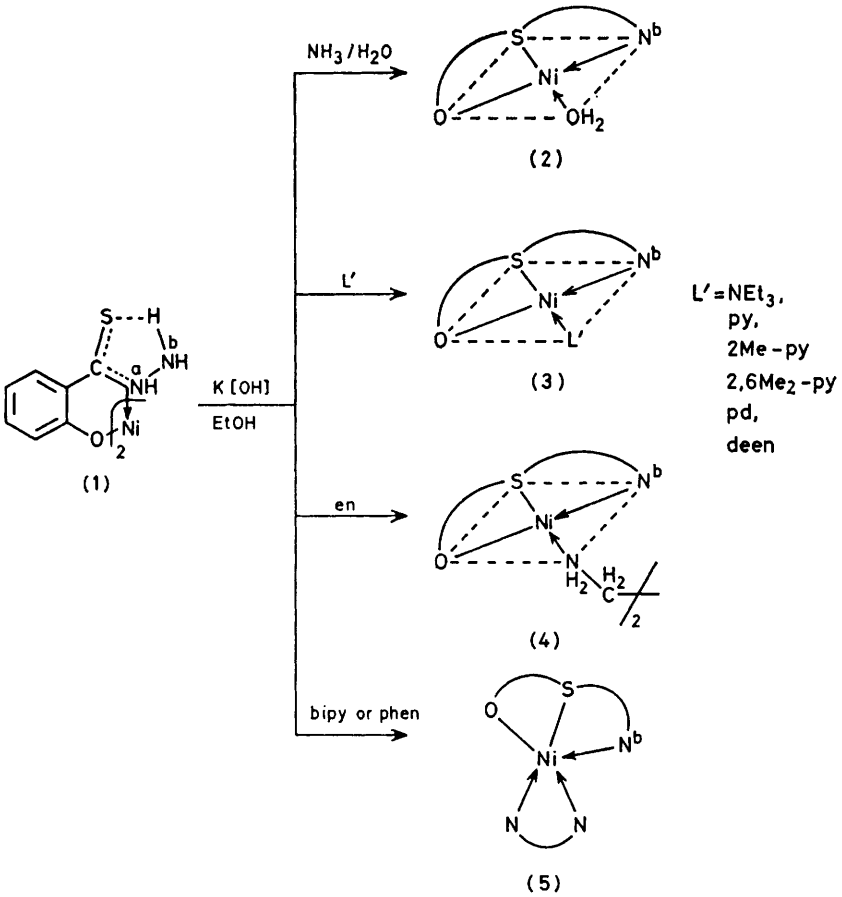
[a] Infrared (KBr disc, 400—4 000 cm^{-1}), far-i.r. (Polythene disc, 100—400 cm^{-1}). vs = Very strong, m = medium, br = broad, (sh) = shoulder, w = weak, vw = very weak. [b] ν(NH_3^+). [c] ρ_w(HOH) at 650w,br cm^{-1}. [d] In-plane ring deformation of pyridine at 645m cm^{-1}. [e] Out-of-plane ring deformation of pyridine. [f] Contribution due to bipy also. [g] Contribution due to phen also. [h] $\delta_s(CH_3)$. [i] The absorptions at 1 060 (sh) and 1 045m cm^{-1} are due to dmso. [j] δ(HOH) at 1 620s and ρ_w(HOH) at 660m,br cm^{-1}. [k] δ(HOH) at 1 630m cm^{-1}; the vibrations at 1 095vs, 1 070s, and 1 035s cm^{-1} are due to the bisulphate group.

absorption band beyond 12 500 cm^{-1}, which indicates that the structures are rigid, possessing probably square-planar geometry even in polar solvents.[22-24] The lowest energy band is presumed to be due to *d–d* in combination with a charge-transfer (c.t.) transition. The assignment of this *d–d* transition is based on the assignment of $Ni^{II}(N_2O_2)$ [25] and $Ni^{II}(N_2S_2)$ [26] chromophores because the [NiLL'] complexes possess $Ni^{II}(N_2OS)$ or $Ni^{II}(NO_2S)$ chromophores. The assignments of the closely spaced absorption bands to c.t. are made on the basis of the assignments of square-planar nickel(II) complexes made by Gray and Ballhausen [27] and Chaston and Livingstone.[28]

On the other hand, if both NH_3 and H_2O are added to an ethanolic K[OH] solution of (1) the diamagnetic red complex [$NiL(OH_2)$] (2) is generated in preference to [$NiL(NH_3)$]. The presence of three distinct bands at *ca.* 3 300 cm^{-1} and a weak broad band at 650 cm^{-1} (Table 3) is expected to be due to the vibrations of co-ordinated water.[29] Hydrogen-1 n.m.r. spectral data (Table 2) also support the presence of the water molecule. The absorption spectrum of the compound in acetone is similar to that of [$NiL(NEt_3)$] in dmso which definitely points to the rigid square-planar geometry attained in [NiLL'] complexes. This is also supported by the presence of sharp signals [30] in the ^1H n.m.r. spectra run in a co-ordinating solvent like [$^2H_5$]pyridine because, in general, sharpness disappears on the development of paramagnetism due to solvent co-ordination.

Reaction of Bidentate Heterocyclic Nucleophiles with [$Ni(HL)_2$].—The reaction of (1) with bipy or phen under similar conditions to those above generates deep brown compounds. These are five-co-ordinate [structure (5)], as the absorption spectra of [NiL(bipy)] and [NiL(phen)] fit well with the spectra of complexes having either C_{3v} or D_{3h} and C_{4v} symmetry [31] respectively, and the bands are assigned accordingly. Magnetic moments also support five-co-ordination. However, it is prudent to comment on the exact symmetry from only absorption spectra as the absorption spectra of square-pyramidal and trigonal-bipyramidal symmetry closely resemble one another in general appearance.[32] On comparison of i.r. spectra of (1) with [NiL(bipy)], it appears that a band at 1 445 cm^{-1} for (1) becomes intensified for the latter, which is probably due to the presence of bipy in the system.[33] An extra band at 847 cm^{-1} in [NiL(phen)] can be assigned to phen.[33] The bands in the lower-frequency region at 200—300 cm^{-1} are attributed to ν(M-N)(bipy or phen) vibrations.[34,35]

Reaction of Aliphatic Diamines with [$Ni(HL)_2$].—The treatment of (1) with pd and deen in ethanolic K[OH] afforded deep red diamagnetic [NiL(pd)] and [NiL-



SCHEME 1

TABLE 4

Electronic spectral data (cm^{-1}) of complexes derived from bis(thiosalicylohydrazidato)nickel(II)

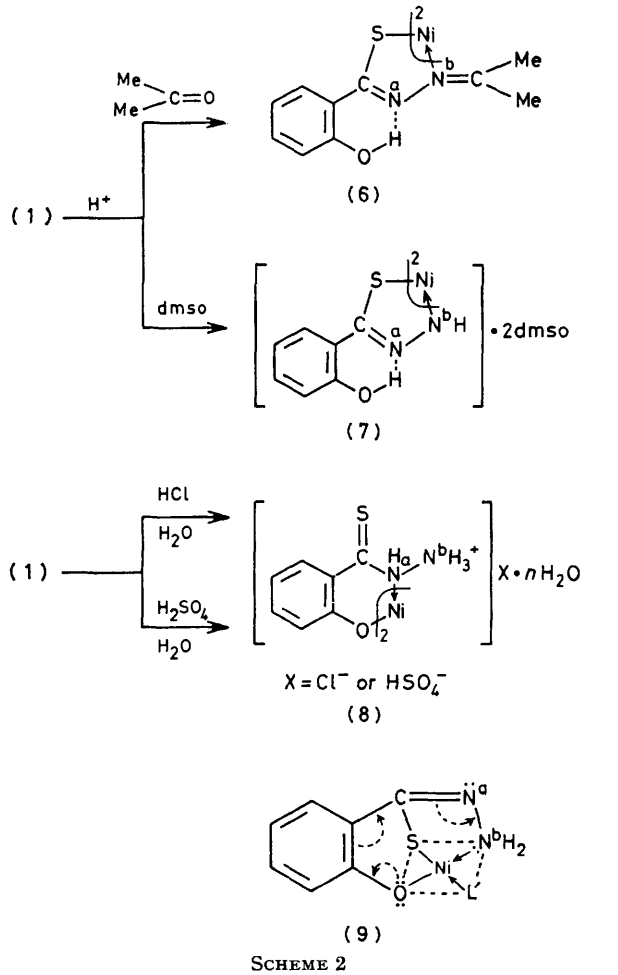
Compound	Absorbance maxima/cm^{-1} (ϵ/dm^3 mol^{-1} cm^{-1})	Tentative assignment
$[Ni(HL)_2]$ [a]	10 638 (200), 12 820 (400), 18 182 (sh) (110), 20 080 (sh) (150), 22 727 (sh) (260)	$^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}$, $^3A_{2g}\rightarrow{}^1T_{1g}(P)$, c.t. + $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ (?)
$[NiL(OH_2)]$ [b]	21 186 (6 500), 22 727 (sh) (7 450), 23 697 (8 800), 24 691 (8 550)	$(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g\rightarrow{}^1B_{1g})$ (?), $M_d\rightarrow L_{\pi}^*$, $M_d\rightarrow L_{\pi}^*$, $L_{\pi}\rightarrow M_d$
$[NiL(NEt_3)]$ [a]	20 833 (6 700), 22 057 (sh) (6 950), 23 041 (7 700), 24 272 (sh) (6 450)	$(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g\rightarrow{}^1B_{1g})$ (?), $M_d\rightarrow L_{\pi}^*$, $M_d\rightarrow L_{\pi}^*$, $L_{\pi}\rightarrow M_d$
$[NiL(py)]$ [a]	21 053 (6 300), 22 371 (8 200), 23 529 (7 700)	$(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g{}^1\rightarrow{}^1B_{1g})$ (?), $M_d\rightarrow L_{\pi}^*$, $L_{\pi}\rightarrow M_d$
$[NiL(2Me\text{-}py)]$ [a]	21 053 (6 400), 22 371 (8 350), 23 529 (7 600)	$(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g\rightarrow{}^1B_{1g})$ (?), $M_d\rightarrow L_{\pi}^*$, $L_{\pi}\rightarrow M_d$
$[NiL(2,6Me_2\text{-}py)]$	21 053 (6 550), 22 371 (11 100), 23 364 (7 800)	$(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g\rightarrow{}^1B_{1g})$ (?), $M_d\rightarrow L_{\pi}^*$, $L_{\pi}\rightarrow M_d$
$[NiL(bipy)]$ [a]	9 804 (16), 12 195 (31), 20 921 (5 700), 22 472 (7 250), 23 529 (sh) (6 800)	$^3B_1(F)\rightarrow{}^3A_2(F)$, $^3B_1(F)\rightarrow{}^3B_2(F)$, c.t. + $^3B_1(F)\rightarrow{}^3E_2(F)$ (?), c.t. + $^3B_1(F)\rightarrow{}^3A_2(P)$ (?), c.t.
$[NiL(phen)]$ [a]	10 870 (96), 11 905 (100), 17 699 (sh) (570), 20 833 (sh) (3 100), 23 529 (5 500)	$^3E'(F)\rightarrow{}^3A_2(F)$, $^3E'(F)\rightarrow{}^3A_1(F)$, $^3E'(F)\rightarrow{}^3A_2(F)$, c.t. + $^3E'(F)\rightarrow{}^3E''(P)$ (?), c.t. + $^3E'(F)\rightarrow{}^3A_2(P)$ (?)
$[Ni_2L_2(en)]$ [a]	20 833 (1 010), 23 810 (sh) (1 590), 24 691 (1 690)	$(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g\rightarrow{}^1B_{1g})$ (?), $M_d\rightarrow L_{\pi}^*$, $M_d\rightarrow L_{\pi}^*$
$[NiL(pd)]$ [a]	20 833 (5 850), 21 979 (sh) (5 700), 23 256 (7 000), 24 390 (6 000)	$(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g\rightarrow{}^1B_{1g})$ (?), $M_d\rightarrow L_{\pi}^*$, $M_d\rightarrow L_{\pi}^*$, $L_{\pi}\rightarrow M_d$
$[NiL(deen)]$ [c]	21 277 (6 700), 22 727 (sh) (6 550), 23 810 (7 200), 24 691 (sh) (6 350)	$(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g\rightarrow{}^1B_{1g})$ (?), $M_d\rightarrow L_{\pi}^*$, $M_d\rightarrow L_{\pi}^*$, $L_{\pi}\rightarrow M_d$
$[Ni(HL\cdot acetone)_2]$ [c]	19 608 (sh) (390), 23 256 (sh) (3 800)	$^1A_g\rightarrow{}^1B_{1g}$, $(M_d\rightarrow L_{\pi}^*)$ + $(^1A_g\rightarrow{}^1B_{3g})$ (?)
$[Ni(HL)_2]\cdot 2dmso$ [d]	10 870 (sh) (900), 13 230 (1 900), 18 182 (sh) (420), 20 802 (sh) (520), 22 222 (sh) (520	$^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}$, $^3A_{2g}\rightarrow{}^1T_{1g}(P)$, c.t. + $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ (?)
$[Ni(H_2L)_2]Cl_2\cdot 5H_2O$ [a]	12 500 (30), 18 519 (sh) (30), 23 810 (sh) (170)	$^1A_g\rightarrow{}^1B_{1g}$, $^1A_g\rightarrow{}^1B_{3g}$
$[Ni(H_2L)_2][HSO_4]_2\cdot 2H_2O$ [a]	12 903 (430), 21 277 (sh) (450), 23 256 (sh) (550)	$^1A_g\rightarrow{}^1B_{1g}$, $^1A_g\rightarrow{}^1B_{3g}$

[a] In dmso. [b] In acetone. [c] In chloroform. [d] In dmf.

(deen)], structure (3). [NiL(deen)] is soluble in chloroform while [NiL(pd)] is moderately soluble in polar solvents. The non-shift of the signals of methyl and methylene groups and the downfield shift of the NH_2 signal of deen on complex formation infers the involvement of this nitrogen atom in bonding with the metal ion. Bonding (O,N^b,S) of H_2L to Ni^{II} also takes place in these two complexes. The presence of $\nu(NH_2)$ at 3 350 cm^{-1} and $\rho_w(NH_2)$ at 920 cm^{-1} of [NiL(pd)] in the i.r. spectrum suggests that one NH_2 group of pd probably does not take part in co-ordination. The bands at *ca.* 390 and *ca.* 280 cm^{-1} are probably due to ν(M-N) from M-L' (L' = deen or pd).[36] Both the chelates show identical absorption spectra like $[NiL(OH_2)]$, indicating square-planar geometry.

On the other hand, the treatment of en with the ethanolic K[OH] solution of $[Ni(HL)_2]$ leads to diamagnetic $[Ni_2L_2(en)]$ (4). The absorption spectrum of this compound is similar to that of [NiL(pd)]. The thiosalicylohydrazide ligand shows identical bonding character (O,N^b,S) to that in [NiLL']. While the involvement of both nitrogen atoms of en in bonding can be inferred from the comparison of i.r. spectra,[37] extra bands at 1 339, 1 278, 1 140, 1 008, and 792 cm^{-1} are similar to those of some known en-bridged systems.[38,39]

Reaction of Acetone with $[Ni(HL)_2]$ *in the Presence of Lewis Acid.*—The $[Ni(HL)_2]$ suspension in acetone slowly dissolves on addition of dilute $HClO_4$. On standing, the brownish green solution gives diamagnetic brown crystals which are soluble in chloroform and do not show $\nu(NH_2)$ or $\rho_w(NH_2)$ in the i.r. spectrum, indicating the condensation to have occurred between a free amino-group of $[Ni(HL)_2]$, and the ketonic group of acetone. The presence of a vibrational absorption band at *ca.* 1 480 cm^{-1} may be due to $\delta_{asym.}(CH_3)$.[13] The ^1H n.m.r. spectrum exhibits two singlets separated by 0.4 p.p.m. due to the presence of magnetically non-equivalent Me groups developed by the hindered rotation between N^b and C,



SCHEME 2

which confirms the Curtis type condensation product.[7] Had (N^a,O) bonding existed in the condensed product, then the two singlets for Me groups would have been separated by *ca.* 0.1 p.p.m. as has been observed for the two Me groups of N^a–N^b=CMe_2 in an analogous organic compound.[17] The presence of a signal due to a hydrogen-bonded *ortho*-hydroxy group in the ^1H n.m.r. spectrum precludes any M-O bonding. The above observations lead to the conclusion that the magnetically non-equivalent character of Me groups is comparatively high, as in (6) where (N^b,S) sites are involved in bonding. This is also evident from i.r. spectral data (Table 3). The role of acid is probably to assist the breakage of M-N^a and M-O bonding, resulting in the rearranged product (6). The absorption bands of the compound (Table 4) are ascribed to a *d-d* transition derived from the $Ni^{II}(N_2S_2)$ chromophore in square-planar geometry based on D_{2h} microsymmetry,[26] in which the higher-energy band with high intensity seems to be due to the admixture of c.t. and *d-d* transitions.

Formation of the Adduct $[Ni(HL)_2]\cdot 2dmso$ *in Presence of Lewis Acid.*—On addition of sulphuric acid to a solution of $[Ni(HL)_2]$ in dmso, shining pink crystals separate out. These are diamagnetic and correspond to the formulation $[Ni(HL)_2]\cdot 2dmso$ based on analytical data. The presence of one shoulder at 1 060 cm^{-1} and a medium intensity band at 1 045 cm^{-1} suggest the non-involvement of dmso in co-ordination.[40] The ^1H n.m.r. spectrum (in CCl_4) shows that the position for the Me signal does not alter with respect to that of dmso.[17] This observation supports the presence of non-co-ordinated dmso. The negative shift of $\nu(NH_2)$, the positive shift of $\beta(NH_2)$, and the appearance of ν(CS) as observed for ligand (H_2L), and the absence of ν(SH) suggest the (S,N^b) bonding, structure (7). A peak of δ 13.0 p.p.m. in the ^1H n.m.r. and a broad band at *ca.* 3 400 cm^{-1} in the i.r. spectra are attributable to the hydrogen-bonded hydroxy group which nullifies the M-O bonding as observed in (1). The suggested structure (7) indicates that the same type of rearrangement observed in the preparation of $[Ni(HL\cdot acetone)_2]$ has also taken place here. The absorption spectrum of the adduct (Table 4) in dmf is very similar to that of $[Ni(HL)_2]$ in dmso.[5] However, the absorption coefficients are high, which implies that all *d–d* transitions are coupled with c.t. transitions.

Reaction of Mineral Acids with $[Ni(HL)_2]$.—The interaction of hydrochloric or sulphuric acid with (1) in a water suspension gives a brick-red diamagnetic product. The analytical and conductance data correspond to a formulation $[Ni(H_2L)_2]Y_2$ (Y = Cl^- or HSO_4^-), structure (8). The behaviour of the salts as 1 : 1 electrolytes is probably due to ion-pair formation in solution. This electrolytic behaviour suggests that these two compounds are simply the acid salts of $[Ni(HL)_2]$ as evident from the reversibility of acid salts on exhaustive treatment with water. The above observation excludes the possibility that disproportionation might occur.[2,3] The very broad band at *ca.* 3 400 cm^{-1} is due to the water molecule. Another broad band in the region 2 800—3 100 cm^{-1} indicates $\nu(NH_3^+)$ in the complexes.[3] A few distinct and strong bands in the region 1 000—1 150 cm^{-1} are probably due to the vibrations HSO_4^- of the sulphuric acid salt. The possibility of formation of octahedral geometry in solution is not pronounced like (1), as is evident from the absence of any band beyond 12 500 cm^{-1} in the co-ordinating solvent.[22] The assignment of the bands is based on a square-planar nickel(II) complex [4r] having sulphur-containing ligands, where the lower-energy band appears in almost the same position as for the acid salts.

Conclusions.—It appears from the foregoing discussion that bonding occurs through (O,N^b,S) sites in all the complexes [NiLL'] and $[Ni_2L_2L']$. It is interesting to note that $[NiL(OH_2)]$ is formed instead of $[NiL(NH_3)]$ in the presence of ethanolic K[OH] and concentrated ammonia. The mode of bonding of the nucleophiles to the metal ion is explained on the basis of nucleophilic reactivity order as well as the basic nature of the nucleophiles; the nucleophilic reactivity order py > aniline ~ olefin ~ NH_3 ~ Cl^- > H_2O > OH^- for square-planar complexes of platinum(II) has been established earlier.[42,43] As nickel(II) is on the borderline between hard and soft acid,[44] it selects H_2O among OH^-, H_2O, and NH_3 nucleophiles which are present in the system. But the formation of [NiLL'] with heterocyclic unidentate or bidentate nucleophiles is preferred as those nucleophiles are of the π-acceptor type and they possess delocalised π orbitals as well as vacant π orbitals in addition to lone pairs which cause a synergic effect [45] and enhance the bonding order between metal ion and nucleophile. The synergic effect probably plays an important role in the formation of high-spin five-co-ordinate complexes with bipy and phen. On the other hand, en, pd, and deen form square-planar complexes instead of adopting five-co-ordination, possibly due to the absence of a synergic effect, and this rules out the general trend of formation of a more stable five-membered aliphatic chelate ring with en than a six-membered chelate ring with pd.[46] Surprisingly, however, en bridges two metal ions. On the other hand, pd fails to behave as en which may be due to lengthening of the hydrocarbon chain. In the case of deen, the steric interaction is greater than the inductive effect; [47,48] this inhibits either chelation or bridging.

The ^1H n.m.r. spectra of [NiLL'] complexes exhibit a signal for the N^bH_2 protons at abnormally high field in comparison to those of $[Ni(HL)_2]$. It is generally observed [49] that any group sterically held above or below the plane of an aromatic ring is abnormally shielded because of the ring current effect. Despite the absence of a classical benzene-type ring system, some compounds [49] can exhibit aromatic character based on the fact that abnormally high shielding of a group present in the system is developed owing to a heavy ring current. Similar abnormally high shielding of N^bH_2 seems to have occurred in the diamagnetic [NiLL'] complexes, although classical aromaticity is not present here. However, C=N^a is conjugated with the benzene ring and the N^b nitrogen atom donates electrons to the metal;

the π-electron clouds of C=N^a spread to nitrogen causing a delocalisation along C ··· N^a ··· N^b which supports the existence of (O,N^b,S) atoms in the same plane, as shown in structure (9). The fourth co-ordinating site is taken up by the incoming nucleophile (L') to make a rigid square-planar structure. Therefore, it seems that the steric rigidity as well as the delocalisation in the complex have developed a ring current which opposes the applied magnetic field, resulting in abnormal shielding of the N^bH_2 group.

Moreover, it can be mentioned that the order of deshielding of the N^bH_2 group in the ligand (H_2L) is dependent on the nucleophilic character of NEt_3 and H_2O ($NEt_3 > H_2O$).

We could measure the ^1H n.m.r. spectra of only two complexes, [NiL(NEt_3)] and [NiL(OH_2)], in the same solvent. Hydrogen-1 n.m.r. spectra for the complexes [NiL(2,6Me_2-py)], [NiL(deen)] could not be recorded in dmso because of low solubility. Therefore, it would not be prudent to generalise the order of all the nucleophiles for the deshielding of the N^bH_2 group as solvent effects could make this misleading.

[1/120 *Received*, 27*th January*, 1981]

REFERENCES

[1] K. A. Jensen and J. F. Miquel, *Acta Chem. Scand.*, 1952, **6**, 189.
[2] J. Gabel and E. Larsen, *Acta Chem. Scand., Ser. A*, 1978, **32**, 929.
[3] K. A. Jensen and E. Larsen, *Acta Chem. Scand., Ser. A*, 1979, **33**, 137.
[4] K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, 1961, **15**, 1097; 1961, **15**, 1124.
[5] P. K. Biswas and N. Ray Chaudhuri, *J. Chem. Soc., Dalton Trans.*, in the press.
[6] M. Akbar Ali, S. E. Livingstone, and D. J. Philips, *Inorg. Chim. Acta*, 1973, **7**, 179.
[7] N. F. Curtis, *J. Chem. Soc.*, 1960, 4409.
[8] J. Gabel, E. Larsen, and P. Trinberup, *Acta Chem. Scand., Ser. A*, 1977, **31**, 657.
[9] F. Hansen and S. Larsen, *Acta Chem. Scand., Ser. A*, 1977, **31**, 825.
[10] S. Larsen, *Acta Chem. Scand., Ser. A*, 1974, **28**, 779.
[11] J. Gabel, V. Hasemann, H. Henriksen, E. Larsen, and S. Larsen, *Inorg. Chem.*, 1979, **18**, 1089.
[12] P. W. Selwood, ' Magnetochemistry,' 2nd edn., Interscience, New York, 1956.
[13] K. Geetharani and D. N. Sathyanarayana, *Indian J. Chem., Sect. A.*, 1979, **17**, 134.
[14] B. Singh, R. Singh, R. V. Chaudhury, and K. P. Thakur, *Indian J. Chem.*, 1973, **11**, 174.
[16] G. R. Burns, *Inorg. Chem.*, 1968, **7**, 277.
[17] F. A. Bovey, ' N.M.R. Data Tables for Organic Compounds,' John Wiley, New York, 1967, vol. 1, pp. 27, 153, 248.
[18] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.
[19] A. B. P. Lever and B. S. Ramaswamy, *Can. J. Chem.*, 1973, **51**, 1582.
[20] J. R. Allan, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, 1965, **27**. 1305.
[21] J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 1961, 859.
[22] K. Nag and D. S. Joarder, *Inorg. Chim. Acta*, 1975, **14**, 133.
[23] S. K. Mondal, D. S. Joarder, and K. Nag, *Inorg. Chem.*, 1978, **17**, 191.
[24] H. B. Gray, in ' Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker, New York, 1965, vol. 1, p. 239.
[25] S. Yamada, H. Nishikawa, and E. Yoshida, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 994.
[26] B. G. Warden, E. Billig, and H. B. Gray, *Inorg. Chem.*, 1966, **5**, 78.
[27] H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, 1963, **85**, 260.
[28] S. H. H. Chaston and S. E. Livingstone, *Aust. J. Chem.*, 1967, **20**, 1079.
[29] D. M. Adams and P. J. Lock, *J. Chem. Soc. A*, 1971, 2801.
[30] C. J. Jones and J. A. McCleverty, *J. Chem. Soc. A*, 1970, 2829.
[31] L. Sacconi, in ' Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker, New York, 1968, vol. 4, p. 225.
[32] L. Sacconi, P. Nannelli, N. Nardi, and U. Compigli, *Inorg. Chem.*, 1965, **4**, 943; L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, 1966, **88**, 5180.
[33] A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, 1959, **9**, 211.
[34] B. Hutchinson, J. Takemoto, and K. Nakamoto, *J. Am. Chem. Soc.*, 1970, **92**, 3335.
[35] R. Wilde, T. K. K. Srinivasan, and N. Ghosh, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1017.
[36] A. B. P. Lever and E. Mantovani, *Can. J. Chem.*, 1973, **51**, 1567.
[37] A. Sabatini and S. Califano, *Spectrochim. Acta*, 1960, **16**, 677.
[38] D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1959, 3089.
[39] G. Newman and D. B. Powell, *J. Chem. Soc.*, 1961, 477; *Can. J. Chem.*, 1973, **51**, 1567.
[40] D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, 1960, **82**, 6013.
[41] S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, 1964, **86**, 4594.
[42] H. B. Gray, *J. Am. Chem. Soc.*, 1962, **84**, 1548.
[43] D. Banerjea, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, 1957, **79**, 4055.
[44] R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.
[45] F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' 4th edn., John Wiley, New York, 1980, ch. 25, p. 1049.
[46] J. Bjerrum, *Chem. Rev.*, 1950, **46**, 381.
[47] F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, 1952, **74**, 2373, 5243; 1954, **76**, 211.
[48] H. M. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, 1954, 213.
[49] J. R. Dyer, ' Applications of Absorption Spectroscopy of Organic Compounds,' Prentice-Hall, Englewood Cliffs, New Jersey, 1965, p. 82.