Stereochemistry of Bis(salicylaldiminato)metal(II) Compounds. Part I. Bis[*N*-(2,6-dialkylphenyl)salicylideneiminato]nickel(II) Compounds and Five- and Six-co-ordinate Pyridine and Picoline Complexes

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The compounds bis[*N*-(2,6-dimethylphenyl)salicylideneiminato]nickel(II), bis[*N*-(2,6-diethylphenyl)salicylideneiminato]nickel(II), and analogous species with substituents at the 3 and/or 5 positions of the salicyl moiety, strongly prefer the four-co-planar geometry in the solid state and in non-donor solvents. They are forced into tetrahedral structures only by bulky substitution (NO_2, but not Me, OMe, Br, or Cl) at the 3 position of the salicyl moiety; and they do not form six-co-ordinate oligomers as do the *N*-phenyl and 3- and 4-substituted *N*-phenyl compounds. In pyridine and the picolines, however, in spite of bulk steric effects (*B*-strain), they form five- and six-co-ordinate complexes with the bases, to an extent determined by (*a*) the steric effect {Me > Et (on *N*-phenyl); and γ-pic $\geqslant$ py > α-pic}; and (*b*) the electron-withdrawing substituents on the salicyl moiety (NO_2 > OMe > Br $\geqslant$ Cl > Me $\geqslant$ H > 5,6-benzo; and 3- > 5-). Electronic spectra (5—30 10^3 cm^{-1}), bulk magnetic susceptibility, and ^1H n.m.r. data (including paramagnetic shifts) have been used to define structures.

THE stereochemistry of the nickel(II) salicylaldiminates (I) has been widely studied, and most of the presently available data are in several recent reviews.[1-3]

Here we report on the compounds (I) for which R is 2,6-dimethylphenyl and 2,6-diethylphenyl. These substituents have a combination of steric and electronic effects, which are pertinent to two specific stereochemical

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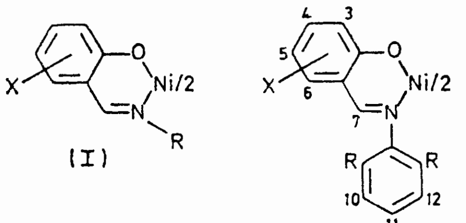
[1] R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83; R. H. Holm and M. J. O'Connor, *ibid.*, 1971, **14**, 241.

[2] S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi, and K. Iawasaki, *Co-ordination Chem. Rev.*, 1968, **3**, 247.

[3] L. Sacconi, *Co-ordination Chem. Rev.*, 1966, **1**, 192; *Transition-Metal Chem.*, 1968, **4**, 199.

problems. (i) The *four co-planar* $\rightleftharpoons$ *tetrahedral* equilibria; and (ii) the formation of five- and six-co-ordinate complexes with donor molecules such as pyridine, as in equilibria (1).



(I) (II)

The numbering is for the identification of the n.m.r. spectra.

$$[NiL_2] + 2B \rightleftharpoons [NiL_2B] + B \rightleftharpoons [NiL_2B_2] \quad (1)$$

During this study, as indicated in a preliminary report,[4] we have isolated for the first time the five-co-ordinate mono-pyridine compounds $[NiL_2B]$ (where B = pyridine or γ-picoline).

A parallel, but less complete study, has been reported by Yamada and his co-workers,[2,5] who did not recognise the five-co-ordinate species.

EXPERIMENTAL

In the general system of abbreviations used for the ligands, substitution on the aniline moiety is indicated by unprimed numbers and on the salicyl moiety by primed numbers. Thus, for example, (2,6-Me_2-3′-NO_2as) refers to the Schiff base derived from 2,6-dimethylaniline and 3-nitrosalicylaldehyde.

2,6-Dimethylaniline and 2,6-diethylaniline, and some of the salicylaldehydes were obtained commercially; but the 3-methyl, 5-methyl, 3-chloro-, 3-bromo-, and 5-bromosalicylaldehydes were prepared from the appropriate phenol by the Reimer–Tiemann procedure.[6] The crude steam-distillates, containing an excess of the phenol, were used for preparing the metal compounds.

Preparation of the Nickel(II) *Compounds*.—The general method of preparation of the bis-bidentate Schiff base compounds was similar to that of Yamada and co-workers.[5] We generally did not measure the quantities of reactants accurately, but mixed the components of the Schiff base in hot methanol, allowing a generous excess of amine, and then added a saturated solution of nickel(II) acetate in water. This was generally followed by $NaHCO_3$ (solid) to neutralise the mixture, which was then digested on a steam-bath for several hours, and the green product was filtered off. It was usually recrystallised from chloroform, often requiring light petroleum for reprecipitation. Where solid pyridine complexes were not formed (see Table 1), a further purification could conveniently be made by dissolving the product in pyridine and reprecipitating by the addition of water.

The compound from 5-nitrosalicylaldehyde and 2,6-dimethylaniline had a very low solubility in the various solvents employed here, and thus is largely excluded from the physical measurements. It was obtained only in small yield.

From the preparations of both compounds of the unsubstituted salicylaldehyde, different crystalline species were obtained and were identified by their *X*-ray powder diffraction patterns. A Table of *X*-ray diffraction data has been deposited in Supplementary Publication No. Sup 20989.

[Ni(2,6-Me_2as)$_2$] (i.) A suspension of [Ni(sal)$_2$(H_2O)$_2$] † in ethanol with an excess of 2,6-dimethylaniline at room temperature gave needles of α-[Ni(2,6-Me_2as)$_2$] after a few days; but they in turn were replaced by prisms of the less soluble [Ni(2,6-Me_2as)$_2$],0·5($C_8H_9NH_2$).

(ii) When a mixture of the amine (2·65 g) and [Ni(sal)$_2$-(H_2O)$_2$] (3·72 g) was refluxed in ethanol (100 ml) for 7 h a considerable amount of the nickel compound remained unreacted. An excess of amine was added, but after further heating (2 h) little further reaction had occurred. The mixture was halved: one half was filtered hot and this gave, on cooling, crystals of α-[Ni(2,6-Me_2as)$_2$] and the amine solvate [Ni(2,6-Me_2as)$_2$],0·5($C_8H_9NH_2$); the other was treated with pyridine (8 ml), and a clear solution formed. When this latter was cooled in the refrigerator (1 h) the α-form was obtained (0·7 g); but the filtrate, when set aside, soon deposited crystals of another species which we label as 'β-[Ni(2,6-Me_2as)$_2$]' (0·8 g).

From subsequent treatments of the filtrate we obtained further quantities of the β-form, some of the amine solvate of the Schiff base compound, and two other products. One of the latter is identified as monoclinic [Ni(sal)$_2$(py)$_2$] {Found: C, 62·4; H, 4·3; N, 5·9. Calc. for $C_{24}H_{20}N_2O_4Ni$: C, 62·8; H, 4·4; N, 6·1%. μ_{eff} = 3·1 B.M. Space group C_c or $C_{2/c}$, a = 14·47, b = 12·16, c = 14·05 Å, β = 116·35°. Mass spectrum peak at m/e = 300 [Ni(sal)$_2^+$]}. The other product is not fully characterised, but is apparently also an Ni(sal)$_2$ species {Found: C, 63·7; H, 4·7; N, 6·3%. Mass spectrum peak at m/e = 300. *X*-Ray powder diffraction lines (2θ for Cu-K_α radiation): 9·3 (m), 12·15 (ms), 13·9 (w), 15·1 (s), 17·25 (w), 17·9 (w), · · · 20·7 (w), 21·1 (w), 21·4 (m), 21·8 (m), 22·3 (m), · · · 30·55 (m), 32·25 (m) · · ·}.

Addition of water to pyridine solutions of α-[Ni(2,6-Me_2as)$_2$], the β-form, or the amine solvate gave only the α-form. The α-form could be recrystallised from $CHCl_3$, but from acetone a monosolvate was obtained which rapidly lost acetone in the air.

[Ni(2,6-Et_2as)$_2$]. When a mixture of [Ni(sal)$_2$(H_2O)$_2$] (4·0 g) and the amine (4·5 g) in ethanol (50 ml) was refluxed for several days the product (6·5 g) was α-[Ni(2,6-Et_2as)$_2$].

A second (β) form was obtained when a pyridine solution of the α-form was set aside to allow the solvent to evaporate. Such a product, however, contains significant amounts of (undefined) hydrolytic material which gives a high-spin octahedral species in pyridine. This led to the initial erroneous conclusion that the β-form gave some octahedral [Ni(2,6-Et_2as)$_2$(py)$_2$] in pyridine.[4] It was obtained in purer form by recrystallising from acetone.

Recrystallisation from various solvents gave either form or mixtures as follows: $CHCl_3$, mixture; acetone, β-form; pyridine, β-form by slow evaporation, and the α-form by precipitating with water; ethanol–pyridine (5 : 1), an excess of the solid in contact with the solution at reflux temperature grew as large crystals of the α-form, but the β-form

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† sal = salicylaldehydate.

[4] D. A. Bone, E. D. McKenzie, and K. Rowan, *Chem. Comm.*, 1970, 420.

[5] S. Yamada, A. Takeuchi, K. Yamanouchi, and K. Iwasaki, *Bull. Chem. Soc. Japan*, 1969, **42**, 131.

[6] D. E. Armstrong and D. H. Richardson, *J. Chem. Soc.*, 1933, 496; H. Wynberg, *Chem. Rev.*, 1960, **60**, 169.

TABLE 1

The compounds prepared and the analytical data

Compound	Found (%)					Calculated (%)			
	C	H	N	Others		C	H	N	Others
(a) Bis-ligand species, and solvates									
[Ni(2,6-Me$_2$as)$_2$] α-form [a]	71·0	5·4	5·6			71·0	5·6	5·5	
[Ni(2,6-Me$_2$as)$_2$] ' β-form '	68·0	5·1	5·8						
[Ni(2,6-Me$_2$as)$_2$],0·5($C_8H_9NH_2$) [b]	71·3	5·9	6·0			71·9	6·0	6·2	
[Ni(2,6-Me$_2$as)$_2$],Me$_2$CO				wt. loss,[c] 11·3					C_2H_6O, 12·7
[Ni(2,3′,6-Me$_3$as)$_2$]	71·1	6·9	5·0			71·7	6·0	6·3	
[Ni(2,5′,6-Me$_3$as)$_2$]	71·6	6·0	5·3			71·7	6·0	5·2	
[Ni(2,6-Me$_2$-3′-MeOas)$_2$] [a]	69·9	6·2	5·3			69·7	5·9	5·1	
[Ni(2,6-Me$_2$-3′-Clas)$_2$]	62·4	4·5	4·7	Cl 12·3		62·5	4·6	4·9	Cl 12·3
[Ni(2,6-Me$_2$-5′-Clas)$_2$] [a]	62·8	4·8	4·8	Cl 12·1		62·5	4·6	4·9	Cl 12·3
[Ni(2,6-Me$_2$-3′,5′-Cl$_2$as)$_2$]	55·4	4·2	4·6	Cl 22·5		55·7	3·9	4·3	Cl 22·3
[Ni(2,6-Me$_2$-3′-Bras)$_2$]	54·3	4·3	4·4	Br 24·2		54·2	4·0	4·2	Br 24·0
[Ni(2,6-Me$_2$-5′-Bras)$_2$] [a]	54·0	3·8	4·4	Br 24·0		54·2	4·0	4·2	Br 24·0
[Ni(2,6-Me$_2$-3′-NO$_2$as)$_2$]	60·2	4·4	8·8			60·3	4·4	9·4	
[Ni(2,6-Me$_2$-3′-NO$_2$as)$_2$],CHCl$_3$				wt. loss,[c] 13·1					$CHCl_3$, 16·7
[Ni(2,6-Me$_2$-5′-NO$_2$as)$_2$] [a]	60·2	4·5	9·3			60·3	4·4	9·4	
[Ni(2,6-Me$_2$-5′,6′-benzoas)$_2$] [a]	74·9	5·6	4·7			75·1	5·3	4·6	
[Ni(2,6-Et$_2$as)$_2$] α-form [a]	72·9	6·4	5·1			72·5	6·4	5·0	
[Ni(2,6-Et$_2$as)$_2$] β-form	72·7	6·3	5·1			72·5	6·4	5·0	
[Ni(2,6-Et$_2$-3′-Meas)$_2$]	73·8	7·2	5·1			73·1	6·8	4·7	
[Ni(2,6-Et$_2$-5′-Meas)$_2$]	73·7	6·7	5·3			73·1	6·8	4·7	
[Ni(2,6-Et$_2$-3′-MeOas)$_2$]	70·0	6·9	4·6			69·4	6·5	4·5	
[Ni(2,6-Et$_2$-3′-Clas)$_2$]	65·0	5·7	4·4	Cl 11·0		64·6	5·4	4·4	Cl 11·2
[Ni(2,6-Et$_2$-5′-Clas)$_2$ [a]	64·7	5·4	4·4	Cl 11·5		64·6	5·4	4·4	Cl 11·2
[Ni(2,6-Et$_2$-3′,5′-Cl$_2$as)$_2$]	58·1	4·6	4·0	Cl 21·1		58·3	4·6	4·0	Cl 20·7
[Ni(2,6-Et$_2$-3′-Bras)$_2$]	57·0	4·8	3·9	Br 22·6		56·6	4·8	3·9	Br 22·2
[Ni(2,6-Et$_2$-5′-Bras)$_2$] [a]	57·2	4·6	3·9	Br 21·9		56·6	4·8	3·9	Br 22·2
[Ni(2,6-Et$_2$-3′-NO$_2$as)$_2$]	62·8	5·4	8·3			62·5	5·3	8·6	
[Ni(2,6-Et$_2$-5′-NO$_2$as)$_2$] [a]	62·7	5·7	8·8			62·5	5·3	8·6	
[Ni(2,6-Et$_2$-5′,6′-benzoas)$_2$] [a]	75·9	6·1	4·1			76·0	6·1	4·2	
(b) Pyridine and picoline complexes									
Ni(2,6-Me$_2$-3′-Clas)$_2$(γ-pic)$_n$ [d]	66·8	5·7	7·4	Cl 9·7	$n = 1$	64·6	5·0	6·3	Cl 10·6
					$n = 2$	66·2	5·3	7·3	Cl 9·3
Ni(2,6-Me$_2$-3′,5′-Cl$_2$as)$_2$(py)$_n$ [d,e]	61·8	4·7	8·3	Cl 14·7	$n = 2$	59·8	4·3	7·0	Cl 17·7
					$n = 3$	61·2	4·5	7·9	Cl 16·1
Ni(2,6-Me$_2$-3′,5′-Cl$_2$as)$_2$(γ-pic)$_n$ [d]	59·3	4·6	6·3	Cl 18·7	$n = 1$	58·6	4·2	5·7	Cl 19·2
					$n = 2$	60·7	4·6	6·7	Cl 17·1
[Ni(2,6-Me$_2$-3′-Bras)(py)$_2$]	58·9	4·6	6·5	Br 19·4		58·4	4·4	6·8	Br 19·4
				wt. loss,[f] 22·3					2py, 19·2
[Ni(2,6-Me$_2$-3′-Bras)(pic)$_2$]	59·0	5·1	6·9	Br 19·0		59·3	4·8	6·6	Br 18·8
[Ni(2,6-Me$_2$-3′-NO$_2$as)(py)$_2$]	62·3	4·8	11·5			63·6	4·8	11·1	
[Ni(2,6-Me$_2$-3′-NO$_2$as)(γ-pic)$_2$]	62·8	5·4	10·7			64·4	5·2	10·7	
[Ni(2,6-Et$_2$-3′-Clas)$_2$(py)]	65·6	5·7	6·2	Cl 9·3		65·8	5·5	5·9	Cl 10·0
				wt. loss,[f] 10·8					1py, 12·1
[Ni(2,6-Et$_2$-3′-Clas)$_2$(γ-pic)]	66·8	6·2	5·9	Cl 9·9		66·2	5·7	5·8	Cl 9·8
[Ni(2,6-Et$_2$-3′,5′-Cl$_2$as)(py)$_2$]	61·1	5·2	6·6	Cl 15·8		61·5	4·9	6·5	Cl 16·5
[Ni(2,6-Et$_2$-3′,5′-Cl$_2$as)(γ-pic)$_2$]	62·6	5·4	6·6	Cl 16·1		62·3	5·2	6·3	Cl 16·0
Ni(2,6-Et$_2$-3′-Bras)$_2$(py)$_n$	59·3	5·1	6·0	Br 20·6	$n = 1$	58·5	4·9	5·2	Br 20·0
					$n = 2$	60·0	5·0	6·4	Br 18·2
[Ni(2,6-Et$_2$-3′-Bras)$_2$(γ-pic)$_2$]	60·7	5·6	6·6	Br 17·6		60·9	5·3	6·2	Br 17·6
[Ni(2,6-Et$_2$-3′-NO$_2$as)$_2$(py)$_2$]	65·1	5·2	11·1			65·1	5·5	10·4	
[Ni(2,6-Et$_2$-3′-NO$_2$as)$_2$(γ-pic)$_2$]	65·5	5·8	10·2			65·8	5·8	10·0	
[Ni(2,6-Et$_2$-5′-NO$_2$as)$_2$(py)]	63·3	5·5	10·3			63·9	5·4	9·6	
[Ni(2,6-Et$_2$-5′-NO$_2$as)$_2$(γ-pic)$_2$]	65·4	5·9	9·8			65·8	5·8	10·0	

[a] These compounds have been reported previously by Yamada and co-workers, refs. 2 and 5. [b] In the Pd series we have obtained two amine solvates. The first (rather insoluble) product, obtained from a reaction mixture containing an excess of amine, was dissolved in pyridine and, when water was added, we obtained crystals of the second solvate. The latter was isomorphous (*X*-ray powder diffraction patterns) with this Ni spp., so the first obtained Pd spp. is probably a mono- or higher solvate. [c] In the air at room temperature. Large crystals were dried between cellulose tissues before weighing. [d] The diffuse reflectance spectra prove that these products are mixtures of significant amounts of both the five-co-ordinate [NiL$_2$B] and six-co-ordinate [NiL$_2$B$_2$] spp. (Tables 2 and 3). [e] The presence in these crystals of more pyridine than is consistent with the co-ordination number defined by the spectra (Tables 2 and 3) is taken to indicate a pyridine solvate. [f] In a desiccator over H_2SO_4 for some months.

crystallised out on cooling; n-hexane, mixture (about equal amounts).

Only one crystalline form each of [Ni(2,6-Me$_2$-5′-Clas)$_2$] and [Ni(2,6-Et$_2$-5′-Clas)$_2$] was obtained from the variety of solvents noted above. We have not checked most of the other species for possible polymorphism, but [Ni(2,6-Me$_2$-3′-NO$_2$as)$_2$] crystallises from CHCl$_3$ as a monosolvate (of the planar species, as proven by the diffuse reflectance spectrum) which soon loses the CHCl$_3$ in the air.

Space groups and unit cell dimensions for a few of the compounds, and *X*-ray powder diffraction patterns for others are listed in Supplementary Publication No. SUP 20989 (7 pp.).*

Pyridine and Picoline Complexes.—All the parent salicylaldiminates were dissolved in pyridine and γ-picoline and precipitated by the addition of water. The solid complexes so obtained are listed in Table 1. Where no addition compound is listed for a particular salicylaldiminate, the parent species was recovered unchanged. The following salicylaldiminates also were recovered unchanged from α-picoline: [Ni(2,6-Me$_2$-3′-Clas)$_2$], [Ni(2,6-Me$_2$-3′,5′-Cl$_2$as)$_2$], [Ni(2,6-Me$_2$-3′-Bras)$_2$], [Ni(2,6-Et$_2$-3′-Clas)$_2$], [Ni-(2,6-Et$_2$-3′,5′-Cl$_2$as)$_2$], [Ni(2,6-Et$_2$-3′-Bras)$_2$], and [Ni(2,6-Et$_2$-5′-NO$_2$as)$_2$]. Both the 3-nitro compounds gave intractable oils, which could not be induced to crystallise.

During the ^{1}H n.m.r. study in chloroform–pyridine it was observed that [Ni(2,6-Et$_2$-5′-NO$_2$as)$_2$] went through a solubility minimum at the 50 : 50 ratio of solvents, where the compound is present largely as the five-co-ordinate species. This may give a useful method for isolating the latter, but has not yet been explored.

Physical Measurements.—The following instruments were used: Unicam SP 700 spectrophotometer for the electronic spectra, with the diffuse reflectance attachment (SP 735) for the solids; Perkin-Elmer 457 for the i.r. spectra (hexachlorobutadiene and paraffin oil mulls); Varian HA 100 or Perkin-Elmer R12 for the ^{1}H n.m.r. spectra; A.E.I. MS 12 or MS 9 for the mass spectra; Phillips 11·46 cm Debye–Scherrer camera with Co-K_α or Cu-K_α radiation for the *X*-ray powder diffraction patterns (samples in 0·2 or 0·3 mm Lindemann glass capillaries).

Magnetic susceptibilities in solution were measured by Evans' [7] ^{1}H n.m.r. method. For the pyridine solutions, the solvent contained 10% tetramethylsilane. A sealed capillary of this mixture was used for the diamagnetic reference signal.

RESULTS AND DISCUSSION

Steric Effects of the Ligands.—In common with the conformation observed in all known crystal structure analyses of *N*-aryl salicylaldiminates, the phenyl plane is expected to be essentially perpendicular to the salicylaldiminate plane. Indeed the alkyl substituents on the phenyl here make it imperative that this be so, although rotation from the perpendicular of up to *ca.* 30° should be possible. In this conformation, the two ligands in (I) can adopt either of the two extremes: a four co-planar or a tetrahedral arrangement of the donor atoms. (The steric effects also will ensure that only the *trans* isomer of the former exists.) Despite the comments of Yamada and co-workers,[2,5] there seem to be no really significant differences in the total steric effects in either configuration. The ligands, however, do provide a significant energy barrier to the *interconversion* of the two configurations.

However, for a substituent other than H in the 3-position of the salicyl moiety, atom over-crowding favours the tetrahedral over the planar configuration, but does not preclude [8] the latter.

The bulkiness of the ligands provides a general inhibition to the addition of other donor molecules such as pyridine. Thus the equilibria (1) will be expected to lie to the left.

Finally, the steric effects should prevent oligomerisation to octahedral paramagnetic species such as occurs [1] in *m*- and *p*- (but not *o*-) substituted *N*-aryl compounds (I), for which a tetrameric ' cubane ' type structure [9] is indicated, since the nitrogens cannot act as bridging atoms. In common with the analogous 2-methylphenyl and 2,5-dimethylphenyl compounds,[10] there is no association of [Ni(2,6-Me$_2$as)$_2$] in chloroform down to 240 K; and accordingly we neglect the possibility of such oligomers in the further discussion

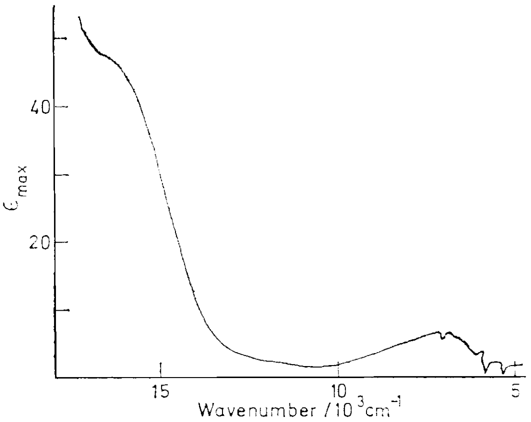

FIGURE 1 The electronic absorption spectrum of [Ni(2,6-Me$_2$-3′-NO$_2$as)$_2$] in CHCl$_3$, showing the band arising from the tetrahedral species at 7 10^3 cm^{-1}

Four-co-planar versus *Tetrahedral Stereochemistry.*—These compounds strongly prefer the four-co-planar geometry, with a diamagnetic ground state.[2,5]

The *electronic spectra* show that [Ni(2,6-Me$_2$-3′-NO$_2$as)$_2$] and [Ni(2,6-Et$_2$-3′-NO$_2$as)$_2$],[1] but only these, give significant concentrations of the tetrahedral isomers in chloroform. [The latter are characterised by low energy absorptions at 7—8 10^3 cm^{-1} (Table 2 and Figure 1).] However, even these compounds crystallise out as diamagnetic planar species (diffuse reflectance spectra, Table 2).

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

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[8] P. C. Jain and E. C. Lingafelter, *Acta Cryst.*, 1967, **B23**, 127; R. L. Braun and E. C. Lingafelter, *ibid.*, p. 780; V. W. Day, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1968, **90**, 4803.

[9] J. E. Andrew and A. B. Blake, *J. Chem. Soc.* (*A*), 1969, 1456; J. A. Bertrand, A. P. Ginsberg, R. I. Caplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, 1971, **10**, 240.

[10] B. M. Higson and E. D. McKenzie, unpublished data.

Both crystalline forms of $[Ni(2,6\text{-}Et_2as)_2]$ contain planar nickel(II) species, as do the various solvates of the different compounds isolated (Table 1). $[Ni(2,6\text{-}Me_2as)_2],0{\cdot}5(C_8H_9NH_2)$ is isomorphous with the Pd analogue (*X*-ray powder diffraction patterns).

The ^1H *n.m.r. spectra* of all compounds in $CDCl_3$ were recorded and the details deposited in Supplementary Publication No. 20989. They give no evidence for contact or pseudo-contact paramagnetic shifting of the resonances, even in the case of the two $3\text{-}NO_2$ compounds for which the electronic spectra show the presence of quite significant amounts of the tetrahedral paramagnetic isomers. This fits with the indication from molecular models of a significant energy barrier to the planar $\rightleftharpoons$ tetrahedral interconversion, which is apparently sufficient to make the process too slow for the observation of averaged contact shifts. We shall report elsewhere the measurement of a slow interconversion of the structural isomers of $[Cu(2,6\text{-}Me_2as)_2]$.

These spectra are generally unexceptionable and parallel, for example, those of our cobalt(III) salicylaldiminates, except for an upfield shift of 3-H (at τ 4·2—4·6) and the 3-Me resonances (at τ 9·1, *cf.* 5-Me at τ *ca.* 7·9). [The numbering system used for the aromatic protons is shown in formula (II).] These shifts result from the shielding effect of the ring current of the *N*-aryl

TABLE 2

The electronic spectra in the region 30—5 10^3 cm^{-1}. Bands appearing as shoulders are given in parentheses, and the extinction coefficients in square brackets

(a) Diffuse reflectance and non-donor solvents

Compound (II) [a]	Phase	Absorption bands/10^3 cm^{-1}				
R = Me, X = H	Solid	27·6	(24·0)	22·5	21·5	16·3
	$CHCl_3$	30 [b]	(24·5) [2900]	22·6 [5000]	(21·5) [3620]	16·3 [100]
3′-Me	Solid	28 [b]	(23·9)	22·3	21·2	16·2
	$CHCl_3$	29·3 [11,700]	(24·1) [3600]	22·7 [5800]	(21·9) [5000]	(16·0) [82] 15·6 [85]
5′-Me	Solid	28 [b]		22·3 [c]	21·1	15·6
	$CHCl_3$	29·0 [10,500]	(24) [3000]	22·4 [4900]	(21·5) [4200]	15·9 [130]
3′-OMe	Solid	28 [b]	(23·7)	22·3	21·1	15·7
	$CHCl_3$	29·0 [12,300]	(24·2) [4300]	22·7 [6350]	(21·9) [5000]	15·9 [150]
3′-Cl	Solid	30 [b]	(24·0)	22·4	(21·7)	15·9
	$CHCl_3$	30 [b] [12,100]	(24·2) [3500]	22·8 [5600]	(22) [4800]	15·8 [90]
5′-Cl	Solid	28·3		22·2 [c]	21·0	16·2
	$CHCl_3$	29 [12,000]	(24) [3000]	22·5 [5100]	(21·5) [4200]	16·15 [120]
3′,5′-Cl_2	Solid	27·4	(24·0)	22·3	21·2	15·7
	$CHCl_3$		(24)	22·4 [4900]	(21·5) [4200]	15·7 [85]
3′-Br	Solid	29 [b]	(24·1)	22·7	(21·9)	15·8
	$CHCl_3$	>30	(24·1) [4000]	22·7 [5700]	(21·9) [5000]	15·65 [80]
5′-Br	Solid	29 [b]		22·1	20·1	16·2
	$CHCl_3$	28·8 [13,000]		22·5 [4600]	(21·5) [4000]	16·1 [120]
3′-NO_2	Solid	28 [b]		22·8 [c]		16·2
	$CHCl_3$	(28)		22·9 [8700]		(16·4) [60], 7·1 [8]
5′-NO_2	Solid	25·5 [b]		23·6		16·6
5′,6′-Benzo	Solid	27 [b]	(23·1)	22·0	20·7	16·5
	$CHCl_3$	28·4 [16,000]	(27·8)	22·6 [6500]	(21·5) [5000]	16·6 [170]
R = Et, X = H	Solid	28·9 (28)	(24)	22·4	21·3	16·1
	$CHCl_3$	>30		22·65 [4500]	(21·7) [3700]	16·25 [100]
3′-Me	Solid	28·3	(24·0)	22·5	(21·7)	15·6
	$CHCl_3$	29·4 [11,500]	(24·0) [3400]	22·7 [5300]	(21·7)	15·6 [80]
5′-Me	Solid	28·2 [b]		22·3	(21·3)	15·9
	$CHCl_3$	28·7 [10,300]	(24·1) [2900]	22·3 [5100]	(21·4) [4400]	(17) [100], 15·9 [130]
3′-OMe	Solid	28·0	(23·8)	22·3	21·2	15·5
	$CHCl_3$	29 [b] [11,300]	(24) [3000]	22·7 [4800]	(21·6) [3600]	15·75 [130]
3′-Cl	Solid	28·4 [b]	(24·0)	22·6	21·6	15·7
	$CHCl_3$	>30	(24·2) [3400]	22·7 [5200]	(21·5) [4600]	15·8 [80]
	C_6H_6	>30	(24·2) [3200]	22·7 [4900]	(21·5) [4300]	15·8 [66]
5′-Cl	Solid	28·5 [b]		22·1 [c]	20·8	16·1
	$CHCl_3$	29 [13,800]		22·4 [c] [4800]	(21·3) [4000]	16·1 [130]
3′,5′-Cl_2	Solid	28·0 [b]	(23·8)	22·3	21·1	15·6
	$CHCl_3$	29·3 [15,000]		22·3 [5300]	(21·4) [4700]	15·6 [110]
3′-Br	Solid	28·7 [b]		22·4 [c]	(21·7)	15·4
	$CHCl_3$		(24·0) [4100]	22·5 [5800]		15·6 [90]
	C_6H_6		(24·0) [3800]	22·7 [5000]		15·7 [70]
5′-Br	Solid	28·0 [b]		22·1 [c]	20·8	16·2
	$CHCl_3$	28·8 [11,500]		22·5 [5100]	(21·3) [4300]	16·15 [140]
3′-NO_2	Solid			22·7 [c]		16·1
	$CHCl_3$		23·4 [13,000]			15·8 [45], 7·6 [6]
5′-NO_2	Solid		*d*			16·8
	$CHCl_3$	(27·0) [21,200]	25·6 [23,000]			16·7 [176]
5′,6′-Benzo	Solid	27·0 [b]	(24)	21·9	20·7	16·5
	$CHCl_3$	(28·3) [21,000]		22·5 [6400]	(21·4) [5000]	16·6 [160]

TABLE 2 (*Continued*)

(b) Pyridines and picolines

Compound (II)	Base	Absorption bands [e]			Other bands	
		(**4**)	(**6**)	(**5**)		
R = Me, X = H	Pyridine	16·2 [104]		5·1 [10]		
	γ-Picoline	16·2 [70]	9·6 [3] [f]	5·3 [12]	(12·7) [4]	11·6 [sp, 3]
3′-Me	Pyridine	15·8 [53]		5 [26]		
	γ-Picoline	15·7 [50[	9·7 [5]	5·2 [28]	(12·9) [8]	11·6 [sp, 5]
5′-Me	Pyridine	16·1 [140]		5·1 [7]		
	γ-Picoline	16·1 [72]	9·6 [2] [f]	5·1 [8]	(12·6) [3]	11·5 [sp, 2]
3′-OMe	Pyridine	15·8 [27]	9·3 [12]		(13·0) [7]	
	γ-Picoline	15·9 [27]	9·2 [13]	6 [2]	(12·8) [7]	
3′-Cl	Pyridine	15·75 [22]	9·3 [13]	5·6 [16]	(12·7) [6]	(11·6) [5]
	γ-Picoline	15·8 [23]	9·3 [12]	5·7 [16]	(12·7) [6]	11·5 [sp, 6]
	α-Picoline	15·9 [60]		5·8 [8]		
5′-Cl	Pyridine	16·0 [56]	9·6 [5] [f]	5·2 [29]	(12·8) [8]	11·6 [sp, 7]
	γ-Picoline	16·0 [59]	9·7 [5] [f]	5·3 [31]	(12·7) [8]	11·6 [sp, 6]
3′,5′-Cl_2	Pyridine	15·6 [20]	9·2 [15]	6 [5]		
	γ-Picoline	16·0 [20]	9·4 [15]	5·5 [7]	12·6 [5]	
	α-Picoline	15·7 [50]	(9) [2] [f]	5·7 [18]	(12·6) [5]	11·6 [sp, 4]
3′-Br	Pyridine	15·6 [14]	9·25 [12]	6·0 [10]	(12·7) [5]	(11·5) [4]
	γ-Picoline	15·6 [20]	9·3 [15]	5·9 [15]	(12·7) [sp, 3]	(11·6) [sp, 3]
	α-Picoline	15·7 [35]	(9) [2] [f]	5·9 [15]	(12·7) [5]	11·6 [sp, 4]
5′-Br	Pyridine	15·8 [62]	9·6 [6] [f]	5·2 [36]	(12·6) [9]	11·6 [sp, 6]
	γ-Picoline	16·0 [54]	9·6 [7] [f]	5·3 [28]	(12·7) [9]	11·6 [sp, 7]
3′-NO_2	Pyridine	*g*	9·8 [18]		(12·9) [8]	
	γ-Picoline	*g*	9·9 [20]		(12·8) [sp, 8]	
	α-Picoline	15·4 [36]	(9·2) [10] [f]	6·3 [30]	12·7 [16]	11·6 [sp, 10]
5′,6′-Benzo	Pyridine	16·6 [135]		5 [4]		
	γ-Picoline	16·7 [130]		6 [4]		
R = Et, X = H	Pyridine	16·2 [100]		5·2 [8]		
	γ-Picoline	16·2 [115]		5·4 [12]	(12·7) [5]	11·6 [4]
3′-Me	Pyridine	15·7 [60]	(9·2) [3] [f]	5·4 [20]	(12·9) [6]	11·6 [sp, 3]
	γ-Picoline	15·7 [50]	(9·2) [4] [f]	5·3 [20]	(12·6) [6]	11·6 [sp, 4]
5′-Me	Pyridine	16·1 [110]		5·1 [5]		
	γ-Picoline	16·0 [90]		5·6 [4]		
3′-OMe	Pyridine	15·7 [24]	9·0 [12]		(12·9) [6]	
	γ-Picoline	15·8 [27]	9·0 [13]		(12·9) [8]	
3′-Cl	Pyridine	15·8 [23]	9·0 [14]	6·0 [15]	12·7 [sp, 7]	11·6 [sp, 6]
	γ-Picoline	15·8 [24]	9·1 [13]	6·0 [15]	(12·7) [sp, 8]	11·6 [sp, 6]
	α-Picoline	15·9 [70]	(9) [2] [f]	6·1 [8]	(11·6) [3]	
5′-Cl	Pyridine	15·9 [63]	(9·2) [4] [f]	5·3 [20]	(12·6) [7]	11·5 [sp, 4]
	γ-Picoline	16·2 [70]	9·4 [5] [f]	5·3 [20]	(12·7) [8]	11·5 [sp, 6]
3′,5′-Cl_2	Pyridine	16·0 [21]	9·2 [15]	(5·7) [6]	(12·7) [5]	(11·4) [5]
	γ-Picoline	16·0 [22]	9·2 [15]	6·2 [10]	(12·7) [7]	(11·5) [6]
	α-Picoline	15·6 [55]	(9) [5] [f]	6·2 [23]	(12·7) [10]	11·6 [sp, 7]
3′-Br	Pyridine	15·6 [17]	9·0 [15]	6·2 [14]	12·7 [sp, 7]	(11·5) [sp, 6]
	γ-Picoline	15·7 [19]	9·1 [13]	6·3 [15]	12·7 [sp, 7]	11·6 [sp, 6]
	α-Picoline	15·5 [45]	(9·2) [5] [f]	6·2 [24]	(12·7) [10]	11·6 [sp, 6]
5′-Br	Pyridine	16·0 [54]	(9·2) [3] [f]	5·3 [18]	(12·5) [6]	11·6 [sp, 4]
	γ-Picoline	16·1 [65]	9·2 [5] [f]	5·6 [20]	(12·7) [8]	11·6 [sp, 6]
3′-NO_2	Pyridine	(16·5) [20]	9·8 [11]		12·7 [2]	
	γ-Picoline	*g*	9·9 [14]		(12·8) [5]	
	α-Picoline	(16·1) [35]	9·7 [14]	6·6 [18]	(12·8) [12]	11·5 [sp, 10]
5′-NO_2	Pyridine	16·4 [23]	9·9 [15]		12·6 [3]	
	γ-Picoline	16·1 [28]	9·7 [14]	6·0 [11]	12·6 [sp, 7]	(11·6) [sp, 8]
	α-Picoline	16·7 [63]		5·9 [17]	(12·8) [5]	11·6 [sp, 4]
5′,6′-Benzo	Pyridine	16·6 [164]		(*ca.* 5?) [<3]		
	γ-Picoline	16·7 [130]		?		

[a] Substitution on the salicyl moiety is indicated by primed numbers. [b] Broad band. [c] Asymmetric to high energy. [d] Broad unresolved absorption between 30 and 20 10^3 cm^{-1}. [e] Here we tabulate in separate columns the data which give evidence for the co-ordination number which heads the column. [f] The five-co-ordinate species also have a low intensity band at *ca.* 9 10^3 cm^{-1}, so there is often an ambiguity as to the possible contribution of a small amount of an octahedral species here. [g] The band here is masked by ligand or metal-ligand absorptions.

substituent (of the opposite ligand) and confirm that the latter is essentially perpendicular to the salicyl moiety.

The spectrum of $[Pd(2,6\text{-}Me_2as)_2]$ was similar to that of the nickel analogue.

Stereochemistry in Donor Solvents.—In pyridine and the picolines these $[NiN_2O_2]$ compounds form two paramagnetic complexes as defined by the equilibria (1). Some, but not all, of these can be isolated as crystalline solids, sometimes as mixtures (Tables 1 and 3).

Various physical measurements give data on the extent of the solution equilibria. (i) The total amount of both paramagnetic species is defined by the magnetic susceptibilities (Table 4). (ii) The electronic spectra give good evidence for the species present and for their structures, but have not yet been refined to give quantitative data on the equilibria. (iii) Paramagnetic shifts of the ^1H n.m.r. spectra also prove that more than one paramagnetic species is formed.

The two high-spin compounds are seen clearly in the

TABLE 3

A summary of the structural data for the complexes with pyridine and the picolines

	Solution data [a]					
Compound (II)*		% Total complex (from χ_M) [b]	Species identified from spectra [c]	Estimated amounts of the various complexes [d]		Solids isolated [e]
R = Me, X = H	(py)	35	4 + 5	5 (35)	4 (65)	4
	(γ-pic)		4 + 5 (+6)	5 (40)	4 (60)	4
3′-Me	(py)	60	4 + 5	5 (60)	4 (40)	4
	(γ-pic)		4 + 5 (+6)	5 (60+)	4 (40−)	4
5′-Me	(py)	28	4 + 5	5 (28)	4 (72)	4
	(γ-pic)		4 + 5 (+6)	5 (30)	4 (70)	4
3′-OMe	(py)	100	(4) + 6	6 (100)		4
	γ-pic)		(4) + 5 + 6	5 (<5)	6 (>95)	4
3′-Cl	(py)	100	5 + 6	5 (40)	6 (60)	4
	(γ-pic)		5 + 6	5 (40)	6 (60)	5 + 6
	(α-pic)		4 + 5	5 (20)	4 (80)	4
5′-Cl	(py)	83	4 + 5 (+6)	5 (80)	4 (20)	4
	(γ-pic)		4 + 5 (+6)	5 (80)	4 (20)	4
3′,5′-Cl_2	(py)	100	5 + 6	5 (10)	6 (90)	5 + 6
	(γ-pic)		5 + 6	5(15)	6 (85)	5 + 6
	(α-pic)		4 + 5	5 (60)	4 (40)	4
3′-Br	(py)	100	5 + 6	5 (35)	6 (65)	6
	(γ-pic)		5 + 6	5 (40)	6 (60)	6
	(α-pic)		4 + 5	5 (60)	4 (40)	4
5′-Br	(py)	77	4 + 5	5 (80)	4 (20)	4
	(γ-pic)		4 + 5	5 (80)	4 (20)	4
3′-NO_2	(py)	100	6	6 (100)		6
	(γ-pic)		6	6 (100)		6
	(α-pic)		4 + 5 (+6)	5 (75)	6 (5) 4 (20+)	*f*
5′,6′-Benzo	(py)	*g*	4 (+5)	5 (<10)	4 (>90)	4
	(γ-pic)		4 (+5)	5 (<10)	4 (>90)	4
R = Et, X = H	(py)	20	4 + 5	5 (20)	4 (80)	4
	(γ-pic)		4 + 5	5 (25)	4 (75)	4
3′-Me	(py)	48	4 + 5	5 (50)	4 (50)	4
	(γ-pic)		4 + 5	5 (55)	4 (45)	4
5′-Me	(py)	13	4 + 5	5 (13)	4 (87)	4
	(γ-pic)		4 + 5	5 (10+)	4 (90−)	4
3′-OMe	(py)	100	6	6 (100)		4
	(γ-pic)		6	6 (100)		4
3′-Cl	(py)	100	5 + 6	5 (35)	6 (65)	5
	(γ-pic)		5 + 6	5 (35)	6 (65)	5
	(α-pic)		4 + 5	5 (20)	4 (80)	4
5′-Cl	(py)	60	4 + 5	5 (60)	4 (40)	4
	(γ-pic)		4 + 5	5 (60)	4 (40)	4
3′,5′-Cl_2	(py)	100	5 + 6	5 (15)	6 (85)	6
	(γ-pic)		5 + 6	5 (25)	6 (75)	6
	(α-pic)		4 + 5	5 (60)	4 (40)	4
3′-Br	(py)	100	5 + 6	5 (35)	6 (65)	5 + 6
	(γ-pic)		5 + 6	5 (35)	6 (65)	6
	(α-pic)		4 + 5	5 (60)	4 (40)	4
5′-Br	(py)	63	4 + 5	5 (50)	4 (50)	4
	(γ-pic)		4 + 5	5 (50)	4 (50)	4
3′-NO_2	(py)	100	6	6 (100)		6
	(γ-pic)		6	6 (100)		6
	(α-pic)		(4+) 5 + 6	5 (45)	6 (55)	*f*
5′-NO_2	(py)	100	6	6 (100)		5
	(γ-pic)		5 + 6	5 (20)	6 (80)	6
	(α-pic)		4 + 5	5 (45)	4 (55)	4
5′,6′-benzo	(py)	*g*	4 (+5)	5 (<5)	4 (>95)	4
	(γ-pic)		4	4 (>95)		4

[a] Results refer to ' room temperature ' (18 ± 3 °C). [b] These were calculated from the data given in the Supplementary publication using a figure of 4150 as the χ_M' for 100% paramagnetic. [c] Numbers are the co-ordination number at the nickel. Parentheses imply an ambiguity about the presence of the particular species (see Discussion section). [d] These figures are rough estimates, based on both the magnetic data given in the Supplementary publication and the intensities of the various bands in the spectra. An $\epsilon_{max.}$ of 40 seems to be about right for the five-co-ordinate species. [e] These are the co-ordination numbers of the solids isolated when water is added to the solutions in the various solvents. [f] The products (see *e*) were intractable oils. [g] Too low to be measured, but the presence of a small amount of the five-co-ordinate species is detected from the ^1H n.m.r. spectra.

* Substitution on the salicyl moiety is indicated by primed numbers.

electronic spectra, such as that of [Ni(2,6-Et$_2$-3′-Bras)$_2$] in pyridine (Figure 3). The bands at *ca.* 9 and 16 10^3 cm^{-1} are quite characteristic of a six-co-ordinate [NiL$_2$B$_2$] species; whilst that at *ca.* 6 10^3 cm^{-1} is a prominent characteristic band of the new five-co-ordinate species which we define here. The full spectrum of the latter is best seen in the diffuse reflectance spectrum of, for example, [Ni(2,6-Et$_2$-3′-Clas)$_2$(py)] (Figure 2), showing that this species also has a band at *ca.* 16 10^3 cm^{-1} (as does any residual diamagnetic four-co-ordinate species that may be present). Thus the bands at *ca.* 10 and *ca.* 6 10^3 cm^{-1}, and only these, can be used to detect the presence of significant amounts of the six- and/or the five-co-ordinate complexes, respectively. They cannot be used to define exactly the equilibria (1) for we do not have any information on absolute extinction coefficients in these solutions; and there is some ambiguity in the detection of small amounts of the six-co-ordinate species in solutions containing mainly the five-co-ordinate species, since the latter appears to have a weak band at *ca.* 10 10^3 cm^{-1} (Figure 2). Still some rough but useful estimates of the relative amounts of each can be given (Table 3).

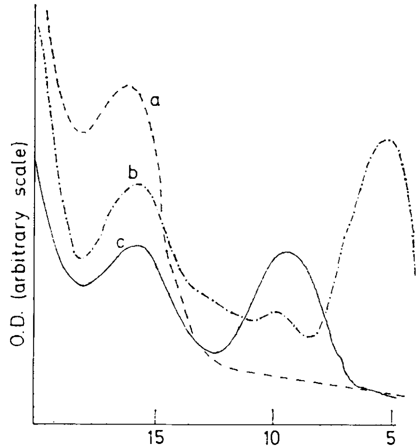

FIGURE 2 The diffuse reflectance spectra of: a, [Ni(2,6-Me$_2$-5′-Bras)$_2$] (four-co-ordinate); b, [Ni(2,6-Me$_2$-3′-Clas)$_2$(py)] (five-co-ordinate); and c, [Ni(2,6-Me$_2$-3′-Bras)$_2$(γ-pic)$_2$] (six-co-ordinate)

TABLE 4

The magnetic susceptibility data for pyridine solutions (*ca.* 20 g l^{-1})

Compound	χ_M	χ_M'	μ_{eff}
R = Me, X = H	1272	1453	1·88
3′-Me	2249	2458	2·44
5′-Me	746	955	1·52
3′-OMe	3867	4084	3·14
3′-Cl	3942	4155	3·17
5′-Cl	3221	3434	2·88
3′,5′-Cl$_2$	3676	3917	3·08
3′-NO$_2$	3897	4088	3·15
3′-Br	3858	4090	3·15
5′-Br	2949	3181	2·78
5′,6′-Benzo	*a*		
R = Et, X = H	613	846	1·43
3′-Me	1754	2010	2·21
5′-Me	304	560	1·16
3′-OMe	3932	4196	3·19
3′-Cl	3874	4134	3·16
5′-Cl	2231	2492	2·46
3′,5′-Cl$_2$	3813	4101	3·15
3′-NO$_2$	3863	4101	3·15
5′-NO$_2$	3951	4189	3·18
3′-Br	3879	4159	3·18
5′-Br	2333	2613	2·52
5,6-Benzo	*a*		

[a] The paramagnetic signal was not resolved from the diamagnetic one.

These assignments of the spectra to five- and six-co-ordinate species are further confirmed by the spectra of Figure 3 (obtained at different temperatures). When the solutions are heated, the equilibria (1) are displaced to the left, so that the five-co-ordinate species becomes more prominent.

Our study of the paramagnetic shifts of the ^{1}H *n.m.r. spectra* was similar to La Mar's study[12] of the compound (I), for which R = Et. By contrast, in our systems, the five-co-ordinate species persist over a much wider range of pyridine concentrations. Figure 4 shows what happens when drops of pyridine (deuteriated) are added to 10 ml of a 0·05M solution of [Ni(2,6-Et$_2$-3′-Bras)$_2$] in CDCl$_3$. The various signals move up or downfield in the order expected for a contact-shift mechanism.[12]

In this range of low pyridine concentrations the paramagnetic shifts change monotonically with pyridine, but, as the latter is further increased, the shifts are no longer monotonic and some of them change direction. Figure 5 gives a plot of signal *vs.* pyridine concentration for [Ni(2,6-Me$_2$-3′-Bras)$_2$] and [Ni(2,6-Et$_2$-5′-NO$_2$as)$_2$] up to the present effective limit of observation. [We have stayed within the range +10 to −20 p.p.m. (w.r.t. tetramethylsilane), and some signals broaden markedly and are lost in the background noise at higher pyridine concentrations.]

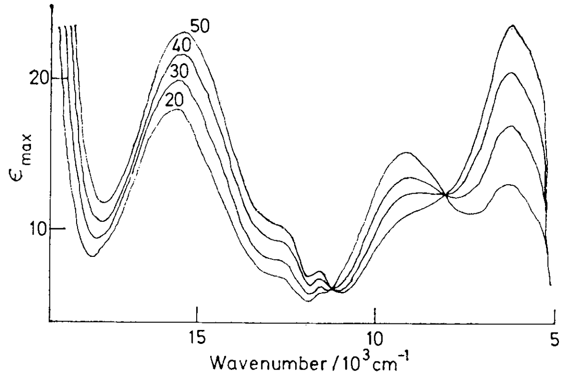

FIGURE 3 The electronic absorption spectra of [Ni(2,6-Et$_2$-3′-Bras)$_2$] pyridine at 20, 30, 40, and 50 °C, as labelled, showing the equilibria between the five- and six-co-ordinate species

The paramagnetic shifts appear qualitatively to be of the normal contact shift type. An exception, however, is apparent in the case of the methylene protons of the ethyl substituted compounds. Figure 4 shows

[11] D. Cummins, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, 1973, 414 and 1359.

[12] G. N. La Mar, *Inorg. Chim. Acta*, 1969, 3, 183.

clearly how the initial quartet collapses into two independent signals, which move down-field at different rates (Figure 5) as pyridine is added. This contrasts with the behaviour of the methyl protons of the 2,6-dimethylaniline compounds, and we currently believe that it results from restricted rotation of the $-CH_2R$ groups, making the two methylene protons non-equivalent in the contact shift mechanisms. Further experiments, including the use of differently substituted anilines and an *X*-ray analysis of a five-co-ordinate solid, should help to distinguish between such a mechanism and an alternative pseudo-contact one.

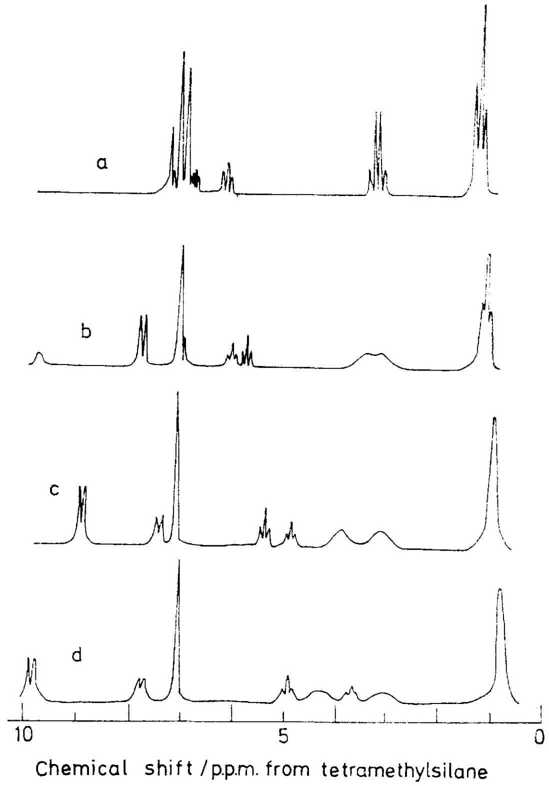

FIGURE 4 The ^1H n.m.r. spectra of $[Ni(2,6\text{-}Et_2\text{-}3'\text{-}Bras)_2]$ in $CDCl_3$ (10 ml) showing the paramagnetic shifts which ensue when drops of C_5D_5N are added as follows: a, no pyridine; b, 1 drop; c, 3 drops; and d, 5 drops

Such ^1H n.m.r. data also are the most powerful in *detecting* small concentrations of the paramagnetic species. At the concentrations available, we cannot use the electronic spectra or the magnetic susceptibilities to detect unequivocally high-spin complexes of the compounds derived from 1-hydroxy-2-naphthaldehyde; but the shifts of some of the ^1H n.m.r. resonances of these compounds in pyridine make it clear that small concentrations of $[NiL_2B]$ are indeed present.

Polymorphism.—Dimorphism and the formation of crystalline solvates are observed, but appear to be uncommon here. We shall discuss elsewhere a greater variety among the cobalt and copper analogues. The various species characterised are given in the Experimental section and in Table 1. Special comments are necessary only for ' β-$[Ni(2,6\text{-}Me_2as)_2]$ '. Mass spectra prove the presence of $[Ni(2,6\text{-}Me_2as)_2]$ and the product can be converted to the α-form by dissolving in pyridine and adding water. However, the *X*-ray molecular weight of 460 is low {507·3 for $[Ni(2,6\text{-}Me_2as)_2]$}; and the electronic spectra (diffuse reflectance) and magnetic susceptibility ($\chi_M = 2093$, $\mu_{eff} = 2{\cdot}2$) suggest a mixed crystal of diamagnetic $[Ni(2,6\text{-}Me_2as)_2]$ and some as yet

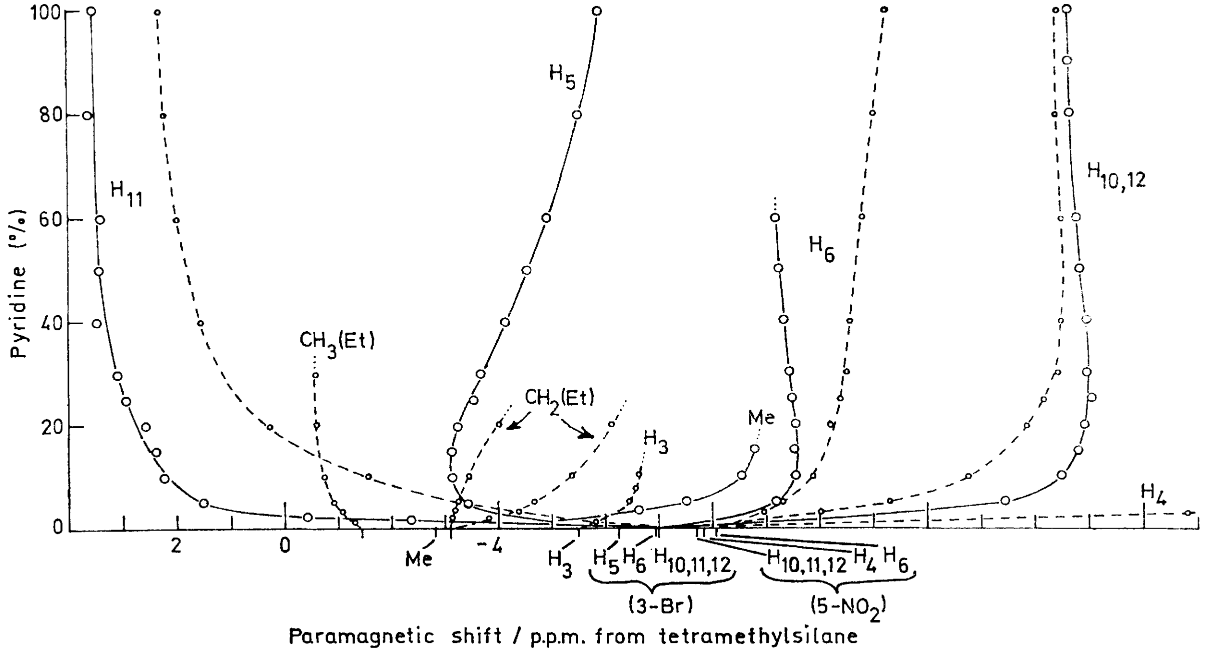

FIGURE 5 Plots of paramagnetic shift *vs.* pyridine concentration (py/$CDCl_3$ mixtures) for the various resonances in $[Ni(2,6\text{-}Me_2\text{-}3'\text{-}Bras)_2]$ (full lines —0·04 g/ml) and $[Ni(2,6\text{-}Me_2\text{-}5'\text{-}NO_2as)_2]$ (broken lines —0·06 g/ml). In each case, H_7 moved to lower field too soon to be representable on this Figure, as did H_4 of the former

undefined high-spin octahedral nickel(II) compound—perhaps a salicylaldehydato-species.

Substituent Effects and Stereochemistry.—The various data pertaining to the five- and six-co-ordinate species are summarised in Table 3. Higher co-ordination numbers are favoured in the following orders: (*i*) Me > Et for the aniline substituent; (*ii*) NO_2 > OMe > Br ⩾ Cl > Me ⩾ H > 5,6-benzo for the salicyl substituents (in positions 3 or 5); (*iii*) 3-substitution > 5-substitution; and (*iv*) γ-pic ⩾ py > α-pic.

Bulk steric effects (*B*-strain[13]) undoubtedly account for both (*i*) and (*iv*); and (*ii*) can be rationalised, at least partly, in terms of the electron-withdrawing power of the ring substituent. The greater the latter, the lower the electron density at the metal atom, which should favour the higher co-ordination numbers (Pauling's electroneutrality principle). Yamada and co-workers[2,5] prefer to argue in terms of the ligand-field strength of the salicylaldiminates, but the two rationalisations are not mutually exclusive. There is no immediately obvious explanation for the observations (*iii*), but they may reflect the entropy part of the total free energy.

We are currently looking further at this problem of the substituent effects, using several series of compounds with the same substituent at positions 3-, 4-, 5-, and 6- of the salicyl ring.

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[13] J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1971, 1666.