Five-co-ordinate Monopyridine-bis(salicylideneiminato)nickel(II) Compounds

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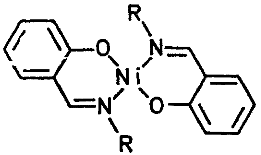
Summary The preparation in solution and in the solid state of five-co-ordinate monopyridine compounds of the bis-salicylidene-2,6-dialkylaniline compounds of nickel(II) is reported.

THE salicylideneiminato-nickel compounds (I) have long been known to form six-co-ordinate compounds [Ni(chel)$_2$L$_2$] in donor solvents such as pyridine.[1-3] Recently, LaMar[4] has detected in solution by ^{1}H n.m.r. techniques, paramagnetic monopyridine compounds of (I; R = Et and Pr^n). We now report the first isolation of solid monopyridine compounds of this type.

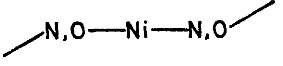
For compounds (I; R = 2,6-Me$_2$C$_6$H$_3$ or 2,6-Et$_2$C$_6$H$_3$), ligand steric effects are expected to favour the formation of monopyridine compounds in this solvent and such cobalt(II) compounds have already been reported.[5] Yamada and his co-workers[2,6] have studied such nickel(II) compounds prepared from various substituted salicylaldehydes, and report that while some of them remain planar in pyridine, others add two pyridine molecules to give six-co-ordinate species. Our results are more extensive, and also give evidence for five-co-ordinate monopyridine species in these systems.

The latter have been detected spectrophotometrically.

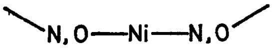
The Figure gives the electronic absorption spectra of $[\mathrm{Ni}\{2,6\text{-}\mathrm{Et_2C_6H_3{\cdot}N{=}CH{\cdot}C_6H_3(O){\cdot}Me\text{-}2,3}\}_2]$ (II) in pyridine and the diffuse reflectance spectrum of the solid monopyridine compound of $[\mathrm{Ni}\{2,6\text{-}\mathrm{Et_2C_6H_3N{=}CH{\cdot}C_6H_3(O){\cdot}Cl\text{-}2,3}\}_2]$ (III).



(I)



(V)



(VI)

These spectra are quite unlike that of an octahedral bispyridine species,[6] which has lower intensity bands at *ca.* 10,000 and *ca.* 16,000 $\mathrm{cm^{-1}}$. The low energy of the first observed band near 5000 $\mathrm{cm^{-1}}$ indicates the presence of a tetrahedral or high-spin five-co-ordinate monopyridine species. We assign the five-co-ordinate geometry since such a spectrum is observed only in good donor solvents, such as pyridine and γ-picoline, and not in benzene, chloroform, or various alkanes. The isolation of several monopyridine species (see Table) with the same spectra is further evidence for this structure.

Although tetrahedral and planar isomers of the copper(II) analogues have been characterised,[7] and dimorphism observed in the tetrahedral cobalt(II) analogues,[7] we have found little evidence for tetrahedral isomers of the planar nickel(II) species. The only possible exceptions are the compounds $[\mathrm{Ni}\{2,6\text{-}\mathrm{R_2C_6H_3{\cdot}N{=}CH{\cdot}C_6H_3(X){\cdot}O\text{-}2}\}_2]$ (IV; X = 3-$\mathrm{NO_2}$) which are planar in the solid, but whose spectra in chloroform solution are different from those of the Figure, having a first absorption band at *ca.* 7000—8000 $\mathrm{cm^{-1}}$. Molecular models indicate that any substitution in the 3-position of the salicylaldehyde moiety should sterically favour the tetrahedral structure. However, in non-donor solvents none of the 3-chloro-, 3-bromo-, 3-methyl-, or 3-methoxy-species gives any evidence for the existence of tetrahedral isomers—neither from their electronic spectra nor their ^{1}H n.m.r. spectra. The latter gave sharp well-defined signals which are typical of planar diamagnetic nickel(II) species and very similar to those of the analogous palladium compounds. These results show the general reluctance of these nickel compounds to adopt a tetrahedral structure.

The Table gives the stereochemistries (assigned from the absorption spectra) for the various compounds in pyridine solution, and for the solids isolated—usually by the addition of water to the pyridine solutions. In several cases only a very small concentration of the five-co-ordinate species is present in equilibrium with the planar species; and in all cases where the six-co-ordinate species predominates in solution, significant absorption near 5000—6000 $\mathrm{cm^{-1}}$ in their spectra appears to indicate the presence of small amounts of the five-co-ordinate species as well.

The differing behaviour in pyridine of the α- and β-forms of $[\mathrm{Ni(2,6\text{-}Et_2C_6H_3{\cdot}N{=}CH{\cdot}C_6H_4{\cdot}O\text{-}2)_2}]$ is an enigma. These are well-characterised dimorphic forms of the planar species, which may be isomers resulting from the dihedral angle between the donor-atom–metal plane and the ligand (salicylaldimine) plane often observed in such compounds.[8] These we call[9] parallel-puckered and oblique-puckered forms which are shown in projection in (V) and (VI) respectively. Different steric effects from the aniline moiety in these isomers could well favour the five-co-ordinate pyridine addition compound of (VI) and a six-co-ordinate bispyridine compound of (V). Indeed some

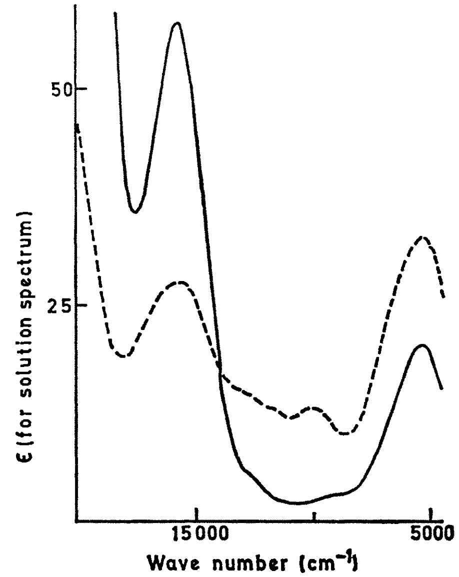


FIGURE. *The electronic absorption spectrum of* (II) *in pyridine* (———), *and the diffuse reflectance spectrum of the solid monopyridine compound of* (III) (– – – –).

TABLE. *The observed stereochemistries of the compounds* (IV) *in pyridine solution, and the solids isolated from pyridine.*

Substituent	Pyridine solution	Solids
R=Me, X=H	4 + 5[a]	4
3-Me	4 + 5	4
5-Me	4 + 5	4
6-Me	4	4
3-OMe	4 + 6	4
3-Cl	4 + 5 + 6	4
5-Cl	4 + 5	4
3,5-$\mathrm{Cl_2}$	6	6
3-$\mathrm{NO_2}$	4 + 6	6
3-Br	5 + 6	6
5-Br	4 + 5	4
5,6-Benzo	4	4
R=Et, X=H (α-form)	4 + 5	4 (α or β)
(β-form)	4 + 6	4 (α or β)
3-Me	4 + 5	4
5-Me	4 + 5	4
6-Me	4	4
3-OMe	4 + 6	4
3-Cl	4 + 5 + 6	5
5-Cl	4 + 5	4
3,5-$\mathrm{Cl_2}$	4 + 6	6
3-$\mathrm{NO_2}$	6	6
5-$\mathrm{NO_2}$	4 + 6	5
3-Br	5 + 6	5 + 6
5-Br	4 + 5	4
5,6-Benzo	4	4

[a] The numbers refer to the co-ordination number of the observed compounds, with 4 referring specifically to planar diamagnetic species.

suggestion of the possible slow interconversion of isomers such as (V) and (VI) is given by the apparent resolution of optical isomers of similar Schiff base planar nickel(II) compounds.[10] Structure (VI) appears to give the only possible origin of such optical activity.

In the present case, however, there is contrary evidence which indicates easy interconversions between the α- and β-"isomers". Recrystallisation under mild conditions from different solvents gives either or both forms, independent of the starting material. However, there is no apparent equilibration of the pyridine solutions. The spectra remain unchanged after several weeks.

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