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Synthesis and Properties of Nickel(II) Complexes with Schiff Bases Obtained from Pyridoxal and Amines

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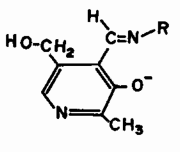
Many nickel(II) complexes have been isolated with Schiff bases obtained from pyridoxal and various monoamines (RNH_2) and polymethylenediamines, and their properties are presented. The 1:2 type complexes were obtained with R = alkyl, aryl and hydroxyalkyl groups. Electronic absorption spectra and magnetic data show that they have a square-planar configuration, except for the complex with R = hydroxyethyl, which is paramagnetic, having a six-coordinate configuration. The 1:1 type complexes were isolated with the Schiff bases obtained from polymethylenediamines. They are diamagnetic and have a planar structure in the solid state. The results are discussed in comparison with those about related complexes.

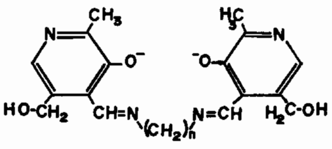
Introduction

In order to obtain basic information, which is expected to be of fundamental importance to discussing the interaction between metal ions and pyridoxal, we recently initiated studies on isolation and characterization of metal complexes with Schiff bases obtained from pyridoxal and reported the results about the copper and cobalt complexes.[1,2]

As continuation of these studies, the present work is concerned with isolation and properties of nickel(II) complexes with the Schiff bases obtained from pyridoxal and such amines as alkyl- and aryl-amines (abbreviated as Pdx-R, I), alkanolamines and polymethylenediamines(II). Very little work has so far been reported about these nickel(II) complexes.



(I)



(II)

Experimental

Pyridoxal hydrochloride of Analar Grade was purchased from Merck and Co. and used as received.

Free pyridoxal was prepared from the hydrochloride, as follows. To a solution of pyridoxal hydrochloride in a small amount of water was added a 20% aqueous solution of sodium hydroxide, the pH being adjusted at about 6.5. A white crystalline precipitate was filtered, washed with cold water, and dried in a desiccator over silica gel.

Bis(N-alkyl- and Bis(N-aryl-salicylaldiminato) nickel(II)

These complexes were synthesized in crystals by the following methods A and B.

Method A

An appropriate amine (0.022 mol) and pyridoxal (0.022 mol) were dissolved in ethanol (100 ml) and heated at about 50–60° C with stirring, until a transparent solution was obtained. Nickel(II) acetate tetrahydrate (0.01 mol) and an aqueous solution of sodium carbonate (0.008 mol) were added to this solution, heated at this temperature for 2–3 hr, and allowed to stand overnight in a refrigerator. A precipitate formed was filtered off, recrystallized from methanol or ethanol, and dried in a desiccator over silica gel.

Method B

An appropriate amine (0.022 mol) and pyridoxal hydrochloride (0.022 mol) were dissolved in ethanol (50 ml) and heated with stirring at about 50° C for about 20 min. To the mixture were added a solution of potassium (0.04 gr. atom) in ethanol (25 ml) and nickel(II) acetate tetrahydrate (0.01 mol) at 50° C, and the resulting solution was heated with stirring at this temperature for 2–3 hr. The solution was allowed to stand overnight in a refrigerator. A crystalline precipitate formed was filtered off and recrystallized from methanol or ethanol.

Bis(N-2-hydroxyethyl- and Bis(N-3-hydroxypropyl-salicylaldiminato)nickel(II)

These complexes were synthesized in crystals by the method A described above, ethanolamine and n-propanolamine being used as an amine component.

Bis(pyridoxal)polymethylenediiminatonickel(II)

These complexes were synthesized in crystals by the method A described above. As an amine component, ethylenediamine, trimethylenediamine and tetramethylenediamine were employed.

Analytical data of the nickel(II) complexes synthesized in the present work are shown in Table I. They are slightly soluble in methanol and ethanol, and almost insoluble in chloroform, water and benzene. The solubility of bis(N-aryl-pyridoxaldiminato)nickel(II) is slightly higher than that of the N-alkyl- and N-hydroxyalkyl- analogues. The complexes with the quadri-

TABLE I. Analytical Data of Nickel(II) Complexes with Schiff Bases Derived from Pyridoxal and Amines.

Complex	Calcd., %			Found, %			Colour
	C	H	N	C	H	N	
Ni(Pdx-CH$_3$)$_2$	51.83	5.32	13.42	51.71	5.51	13.16	green
Ni(Pdx-C$_2$H$_5$)$_2$	53.96	5.89	12.56	54.38	6.06	12.67	green
Ni(Pdx-*n*-C$_3$H$_7$)$_2$[a]	53.79	6.57	11.41	54.10	6.28	11.66	green
Ni(Pdx-*i*-C$_3$H$_7$)$_2$[a]	53.79	6.57	11.41	54.46	6.36	11.64	green
Ni(Pdx-*n*-C$_4$H$_9$)$_2$[a]	55.51	6.99	10.79	55.22	6.48	10.81	green
Ni(Pdx-ph)$_2$	62.13	4.84	10.35	62.55	4.71	10.75	olive
Ni(Pdx-2,6-(CH$_3$)$_2$ · ph)$_2$[a]	62.46	5.90	9.10	62.80	5.65	9.23	olive
Ni(Pdx-2,6-(C$_2$H$_5$)$_2$ph)$_2$[a]	64.39	6.61	8.34	64.68	7.06	8.11	olive
Ni(Pdx-CH$_2$CH$_2$OH)$_2$[a]	48.71	5.31	11.36	48.73	5.43	11.31	orange
Ni(Pdx-CH$_2$CH$_2$CH$_2$OH)$_2$	52.30	5.99	11.09	52.33	5.90	11.15	green
Ni(Pdxen)	52.09	4.86	13.50	51.90	4.88	13.43	orange
Ni(Pdxtn)[a]	51.04	5.41	12.53	51.28	5.19	12.19	orange
Ni(Pdxtet)[b]	53.13	5.57	12.39	53.06	5.41	12.36	olive

[a] 1H$_2$O. [b] $^1/_2$H$_2$O. ph = phenyl; Pdxen = bis(pyridoxal)ethylenediiminate; Pdxtn = bis(pyridoxal)trimethylenediiminate; Pdxtet = bis(pyridoxal)tetramethylenediiminate.

TABLE II. Maxima of Main Electronic Absorption Bands of Nickel(II) Complexes with N-Substituted Pyridoxaldiminates.

Complex	Solvent	ν (logε)[a]
Ni(Pdx-CH$_3$)$_2$	nujol	16.8
	pyridine	10.2 (0.96), 16.7 (0.94)
Ni(Pdx-C$_2$H$_5$)$_2$	nujol	16.5
Ni(Pdx-*n*-C$_3$H$_7$)$_2$ · H$_2$O	nujol	16.6
	pyridine	10.1 (1.12), 17 (1.14) sh
Ni(Pdx-*i*-C$_3$H$_7$)$_2$ · H$_2$O	nujol	16.5
	pyridine	10.2 (1.09)
Ni(Pdx-*n*-C$_4$H$_9$)$_2$ · H$_2$O	nujol	16.5
	pyridine	10.2 (1.18)
Ni(Pdx-ph)$_2$	nujol	16.3
	pyridine	10.2 (1.23)
Ni(Pdx-2,6-(CH$_3$)$_2$ · ph)$_2$ · H$_2$O	nujol	16.2
	pyridine	5.4 (1.53), 15.9 (1.77)
Ni(Pdx-2,6-(C$_2$H$_5$)$_2$ · ph)$_2$ · H$_2$O	nujol	16.2
	pyridine	5.3 (1.40), 16.0 (1.77)
Ni(Pdx-CH$_2$CH$_2$OH)$_2$ · H$_2$O	nujol	11.2, 19.0 sh
Ni(Pdx-CH$_2$CH$_2$CH$_2$OH)$_2$	nujol	16.3
Ni(Pdxen)	pyridine	10.1 (1.11)
Ni(Pdxen)	nujol	18.2 sh
Ni(Pdxtn) · H$_2$O	nujol	17 sh
	pyridine	11.5 (1.35), 12.5 (0.95) sh
Ni(Pdxtet) · $^1/_2$H$_2$O	nujol	15.7

[a] ν: 10^3 cm^{-1}; sh: shoulder.

dentate pyridoxaldiminates are gradually decomposed in organic solvents, although their solubility is very low in most solvents.

Measurements

Electronic absorption spectra of the complexes in solution and in nujol were recorded on a Shimadzu MPS-500 and a Hitachi EPU-2 spectrophotometer. Beer's law was found to hold for all the solution spectra reported in the present paper.

Magnetic measurements were carried out by the Gouy method at room temperature using $CoHg(SCN)_4$ as a calibrant.

Results and Discussion

Bis-type Nickel(II) Complexes

As shown in Table I, the 1:2 type complexes were obtained with N-alkyl-, N-aryl- and N-hydroxyalkyl-pyridoxaldiminates. Since bis(N-alkylpyridoxaldiminato)nickel(II) complexes are diamagnetic in the solid state, they most probably have a planar configuration. As shown in Table II, their electronic absorption spectra in nujol are typical of the planar nickel(II) complexes, showing a *d–d* band at about 16–17 kK, which may be assigned to a $d_{x^2-y^2} \leftarrow d_{xy}$ transition. It is interesting to note that bis(N-isopropylpyridoxaldiminato)nickel(II) in the solid state shows spectrum typical of the planar complex, having a *d–d* band at about 16.2 kK. The complex, therefore, presumably has a square-planar geometry, in spite of the steric hindrance arising from the isopropyl groups. It was previously reported that the structure of bis(N-isopropyl ring-substituted salicylaldiminato)nickel(II) is square-planar or tetrahedral, depending upon the substituents on the benzene rings.[3,4]

The spectra of all the above complexes in pyridine are typical of the six-coordinate octahedral nickel(II) complex, having a *d–d* band at 10.1–10.2 kK. It is thus presumed that in pyridine they exist as six-coordinate bis (pyridine)nickel(II) complexes. The solution spectra in non-donor solvents were not measured because of their low solubility.

Bis(N-arylpyridoxaldiminato)nickel(II) complexes are also presumed to have a planar geometry, since they are diamagnetic in the solid state. Their electronic spectra are similar to each other and typical of the planar nickel(II) complexes, all showing the first *d–d* band at about 16.1–16.3 kK, as may be seen from Table II. The band maxima of their *d–d* bands are nearly the same as those of the corresponding salicylaldiminatonickel(II) complexes,[5] a fact which suggests that the ligand fields produced by these ligands may be almost equal.

It should be noted that they exist solely as four-coordinate, planar complexes in methanol and in ethanol; no equilibrium consisting of various configurations occurs. Thus, in contrast to the salicylaldiminato complexes, no association of the bis(pyridoxaldiminato) nickel(II) complexes takes place in non-donor solvents, where they show no absorption band at about 10 kK, characteristic of the six-coordinate nickel(II) complexes, and Beer's law holds almost strictly. This finding seems to suggest that the ligand field produced by the N-substituted pyridoxaldiminate is higher, though only slightly, than that produced by the corresponding slicylaldiminate, since it is known that the stronger ligand field favours the spin-paired singlet state than the weaker one.

In pyridine, $Ni(Pdx\text{-}ph)_2$ forms a six-coordinate bis (pyridine)adduct. On the contrary, spectra of $Ni(Pdx\text{-}2,6\text{-}(CH_3)_2\cdot ph)_2$ and $Ni(Pdx\text{-}2,6\text{-}(C_2H_5)_2\cdot ph)_2$ in pyridine are different from those of planar and octahedral nickel(II) complexes, but similar to those of the possibly five-coordinate pyridine adducts of the bis (salicylaldiminato)nickel(II) complexes,[6] having a comparatively broad band at about 5.3–5.4 kK (Table II). It is likely that they form five-coordinate mono (pyridine)adducts, when dissolved in pyridine, probably because the steric condition arising from the two alkyl groups at 2- and 6-positions may prevent the nickel(II) ion from forming six-coordinate bis(pyridine)adducts. A similar result was reported in the case of the corresponding bis(salicylaldiminato)nickel(II) complexes.[5,6]

$Ni(Pdx\text{-}CH_2CH_2OH)_2$ is paramagnetic with a moment of 2.87 B. M. in the solid state, and its spectrum is also typical of the six-coordinate octahedral nickel(II) complex (Table II). The ligand $Pdx\text{-}CH_2CH_2OH$ behaves as a terdentate ligand in this complex. On the contrary, $Ni(Pdx\text{-}CH_2CH_2CH_2OH)_2$ is diamagnetic, and its spectrum is typical of the square-planar nickel (II) complex. The ligand $Pdx\text{-}CH_2CH_2CH_2OH$ behaves as a bidentate ligand in this complex, and the hydroxyl group is not bound with the nickel(II) ion, probably due to the steric condition; the longer trimethylene chain disfavours coordination of the terminal hydroxyl group with the central nickel(II) ion.

Nickel(II) Complexes with Quadridentate Pyridoxaldiminates

The complexes Ni(Pdxen) and Ni(Pdxtn) are diamagnetic and their electronic spectra in the solid state are typical of the spectra of the four-coordinate, planar nickel(II) complexes, showing a *d–d* band as a shoulder at about 18.2 kK and 17 kK, respectively (Table II).

Since Ni(Pdxtet) is also diamagnetic, it has an essentially square-planar structure. As the length of the polymethylene chain increases, the steric condition may become unfavorable for retaining the planar configuration around the nickel(II) ion. In fact, the colour (olive) of Ni(Pdxtet) differs remarkably from that of Ni(Pdxen) (red–orange) or Ni(Pdxtn) (brownish red–orange). The solid spectrum of Ni(Pdxtet) has main features typical of the planar nickel(II) complex, showing a resolved band, not as a shoulder, at about 15.7 kK. However, the maximum of its *d–d* band is found to be displaced toward much lower frequencies than that of Ni(Pdxen) (18.2 kK) or Ni(Pdxtn) (17 kK) in the solid state. This finding probably suggests that Ni(Pdxtet) may be distorted, to some extent, from the strictly planar geometry.

Although Ni(Pdxen) and Ni(Pdxtet) are sparingly soluble in pyridine, Ni(Pdxtn) is more soluble in pyridine, where it forms six-coordinate bis(pyridine) adduct, showing the first *d–d* band at about 11.5 kK. This band has a shoulder on the higher frequency side, indicating the band splitting, which is characteristic of *trans*-disubstituted six-coordinate nickel(II) complex and similar to the band splitting observed for *trans*-[Ni(Saltn)(pyridine)$_2$], Saltn being bis(salicylaldehyde)trimethylenediiminate.[7]

Conclusions

The pyridoxaldiminates as ligands form many nickel (II) complexes, whose composition and structure are similar to those of the corresponding salicylaldiminatonickel(II) complexes. The hydroxymethyl group on the pyridine ring and the pyridine nitrogen atom are not coordinated to the nickel(II) ion in the complexes obtained in the present work, although these may play more or less important part in their reactions in solution.

One of the differences between the pyridoxaldiminato- and the salicylaldiminatonickel(II) complexes is found in their solubility. The solubility of the former in organic solvents is considerably lower than that of the latter.

The ligand field produced by Pdx-R, as judged from the *d–d* band maxima, is nearly equal to that of the corresponding salicylaldiminate, abbreviated as Sal-R. However, comparison of the behaviour of Ni(Pdx-aryl)$_2$ in pyridine with that of Ni(Sal-R)$_2$ seems to indicate that Pdx-R produces slightly stronger ligand field than Sal-R.

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