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Nickel(II) Complexes of Schiff Bases Derived from Alkanolamines and Salicylaldehyde and 3-Methoxysalicylaldehyde

Shoichiro Yamada, Yoshio Kuge*[1] and Kuniko Yamanouchi

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka

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Nickel(II) complexes of Schiff bases derived from salicylaldehyde and amines have so far been studied. In the present work, the nickel(II) complexes of *N*-hydroxyalkyl-salicylideneimines and related compounds are taken up, and the behavior of the hydroxyl group as to its coordination with the nickel(II) ion is examined. Bis(*N*-hydroxyalkyl-3-methoxysalicylideneiminato)- and bis(*N*-hydroxyalkyl-salicylideneiminato)-nickel(II) complexes have been prepared in the present work, where R = CH_2CH_2OH, $CH_2CH(CH_3)OH$, $C(CH_3)_2CH_2OH$ and $CH_2CH_2CH_2 \cdot OCH_3$. These complexes, except for the complexes with R = $CH_2CH_2CH_2OCH_3$, in the solid state are hexa-coordinated and show paramagnetism corresponding to two unpaired electrons. They are hexa-coordinated in non-donor solvents, except for the nickel(II) complexes with R = $C(CH_3)_2CH_2OH$, which take a hexa-coordinated configuration in ethanol or methanol, a square-planar configuration in chloroform, and a different configuration in pyridine.

Numerous papers have so far been published concerning nickel(II) complexes of *N*-alkyl- and *N*-aryl-salicylideneimines. In this connection, it is thought to be interesting to take up the nickel(II) complexes of *N*-hydroxyalkyl-salicylideneimines and related compounds, and to examine the behavior of the hydroxyl group as to its coordination with the nickel(II) ion. The present paper describes the results of the investigations about these nickel(II) complexes of the *N*-substituted derivatives of salicylideneimines and 3-methoxy-salicylideneimines (Fig. 1).

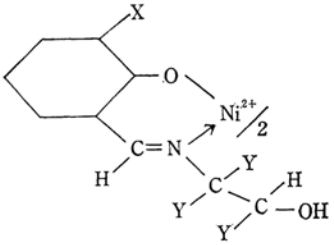

Fig. 1. Ni(X-Sal.R)$_2$, where X = H and 3-CH_3O.

Experimental

Materials. Bis(*N*-hydroxyalkyl-salicylideneiminato)- and bis(*N*-hydroxyalkyl-3-methoxy-salicylideneiminato)-nickel(II)*[2] complexes were prepared by almost the same method as that employed previously.[1,2] A typical procedure is given below. To a mixed solution of nickel(II) acetate tetrahydrate and a slight excess of a ligand (Schiff base) in ethanol was added a calculated amount of an aqueous solution of sodium hydroxide or an ethanolic solution of potassium ethanolate to neutralize the acetic acid which was expected to be liberated in the solution during the reaction. The solution was stirred at 60—70°C for about three hours, and then allowed to stand until its temperature went down to room temperature. After it had been kept for a day at −10°C, the crude product, which separated out, was recrystallized from suitable solvents, such as chloroform, ethanol, benzene and their mixture. Green or yellow-green crystals were obtained.

The new nickel(II) complexes prepared in the present work are those with R = CH_2CH_2OH, $CH_2CH(CH_3)OH$ and $C(CH_3)_2CH_2OH$ for X = H and 3-CH_3O, and one with R = $CH_2CH_2CH_2OCH_3$ for X = 3-CH_3O. The nickel(II) complex with R = CH_2CH_2OH for X = H was previously mentioned briefly, but no detailed discussion about its structure was given.[3,4] Elemental analyses of these complexes are shown in Table 1.

The nickel(II) complexes with R = *t*-C_4H_9, *iso*-C_3H_7, and cyclohexyl for X = H were prepared according to the method previously reported.[1]

Measurements. The electronic absorption spectra of the nickel(II) complexes in solution and the reflectance spectra of the solid were determined with a Shimadzu QR-50 spectrophotometer in the near-infrared, visible and ultraviolet regions at room temperature. Pyridine for a solvent was purified by distillation after having been dried over barium oxide.

Magnetic measurements were carried out by the Gouy method at room temperature.

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*[1] Present address: Osaka Public Health Institute, Morimachi, Higashinari-ku, Osaka.

*[2] Abbreviated in this paper as Ni(X-Sal.R)$_2$, X being 3-CH_3O and H.

[1] S. Yamada and H. Nishikawa, This Bulletin, **36**, 755 (1963).

[2] S. Yamada, H. Nishikawa and E. Yoshida, *ibid.*, **39**, 994 (1966).

[3] G. N. Schrauzer, *Angew. Chem. internation. edit.*, **3**, 185 (1964).

[4] N. Hagihara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **73**, 323 (1952).

Table 1. Elemental analyses of bis(N-substituted salicylideneiminato)- and bis(N-substituted 3-methoxysalicylideneiminato)-nickel(II), Ni(X-Sal.R)$_2$

X	R	mag.mom.*	Calcd, %			Found, %		
			C	H	N	C	H	N
H	CH_2CH_2OH	2.95	55.85	5.21	7.24	55.24	6.00	6.71
	$CH_2CH(CH_3)OH$	3.01	57.87	5.83	6.75	57.86	5.86	6.65
	$C(CH_3)_2CH_2OH$**	2.95	59.46	6.51	6.07	58.64	6.83	5.34
3-CH_3O	CH_2CH_2OH	3.20	53.73	5.41	6.27	52.63	5.55	6.25
	$CH_2CH(CH_3)OH$	3.14	55.61	5.94	5.90	55.40	5.89	5.88
	$C(CH_3)_2CH_2OH$	3.22	57.28	6.41	5.57	57.30	6.49	5.61
	$CH_2CH_2CH_2OCH_3$	dia.***	57.28	6.41	5.57	57.20	6.44	5.53

* solid state (in B. M.). ** with one molecule of water. *** dia.=diamagnetic.

Results and Discussion

It is well known that the electronic absorption spectrum of the nickel(II) complex is dependent upon the configuration of the complex. For Ni(Sal.CH_2CH_2OH)$_2$, the reflectance spectrum of the solid is almost identical with the spectrum of the complex in such non-donor solvents as ethanol and methanol, and the corresponding absorption maxima lie at nearly identical frequencies (Fig. 2 and Table 2). It is concluded, therefore, that Ni(Sal.CH_2CH_2OH)$_2$ in the solid state takes almost the same configuration as in non-donor solvents. Thus the electronic spectrum indicates that the niekcl(II) ion takes hexa-coordination in this complex. The absorption maxima at about 10.7 and 17.0×10^3 cm^{-1} are assigned as $^3T_{2g}\leftarrow{}^3A_{2g}$ and $^3T_{1g}(F)\leftarrow{}^3A_{2g}$, respectively. In order to decide whether the hexa-coordination is due to intermolecular association or to intramolecular combination of the OH-group with the central nickel(II) ion, the molecular weight determination is necessary, but this was not successful due to low solubility of the complexes in suitable solvents. However, since the Beer law is obeyed for the solution, the intermolecular association is excluded, and it is most likely that the intramolecular Ni-OH bond may be present in the complex. Eleven geometric isomers of the two types, the 1, 2, 3- and the 1, 2, 6- form are possible, but the steric condition seems to favor the structure A[5] shown in Fig. 3, although definite conclusion about it may be drawn after X-ray studies.

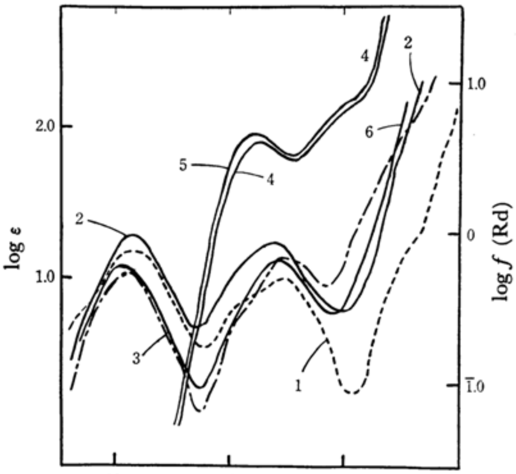

Fig. 2. Electronic absorption spectra of Ni(Sal.R)$_2$: 1, R=CH_2CH_2OH, in the solid state (by reflectance); 2, R=CH_2CH_2OH, in ethanol; 3, R=CH_2CH_2OH, in pyridine; 4, R=C_2H_5, in chloroform; 5, R=$CH_2CH_2CH_2OCH_3$, in $CHCl_3$; 6, R=$CH_2CH_2CH_2OCH_3$, in pyridine.

The complex, Ni (Sal. CH_2CH_2OH)$_2$, in pyridine shows an electronic absorption spectrum characteristic of the hexa-coordinated nickel(II) complex. The band assignment may be made in the same way as given above. It is likely that two pyridine molecules are bound with the nickel(II) ion to replace the two OH-groups, which were originally attached to the nickel(II) ion.

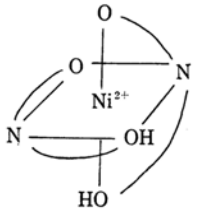

Fig. 3. A prossible molecular structure of Ni(Sal.CH_2CH_2OH)$_2$.

The present work also shows that Ni(3-CH_3O·Sal.$CH_2CH_2CH_2OCH_3$)$_2$ is square-planar in non-donor solvents, and octahedral in pyridine, with two pyridine molecules bound to the nickel(II) ion.

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[5] R. C. Burrows and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 4150 (1966).

TABLE 2. ABSORPTION MAXIMA OF SCHIFF BASE NICKEL(II) COMPLEXES, $Ni(X\text{-}Sal.R)_2$

X	R	Solvent	ν (log ε)	ν (log ε)
H	CH_2CH_2OH	solid	10.7	17.4
		C_2H_5OH	10.7 (1.28)	17.2 (1.24)
		pyridine	10.4 (1.04)	17.3 (1.14)
	C_2H_5	$CHCl_3$	16.3 (1.90)	
	$CH_2CH(CH_3)OH$	solid	10.2	16.3
		C_2H_5OH	10.3 (1.32)	16.6 (1.22)
		pyridine	10.4 (1.04)	17.2 (1.12)
	$C(CH_3)_2CH_2OH$	solid	9.8	15.9
		CH_3OH	10.5 (1.28)	16.9 (1.12)
		pyridine	10.8 (0.75)	17.5 (1.38)*
	$CH(CH_3)_2$	pyridine	10.5 (1.13)	17.2 (1.10)
	cyclohexyl	pyridine	10.0 (1.20)	17.0 (1.07)
$3\text{-}CH_3O$	CH_2CH_2OH	solid	10.6	16.5
		CH_3OH	10.6 (1.16)	16.5 (1.29)
	$CH_2CH(CH_3)OH$	solid	10.3	16.5
		$CHCl_3$	10.3 (1.16)	15.9 (1.40)
		pyridine	10.4 (1.01)	17.4 (1.21)
	$C(CH_3)_2CH_2OH$	solid	9.9	15.8
		pyridine	11.3 (0.51)	17.5 (1.65)*
		CH_3OH	10.4 (1.26)	17.1 (1.30)
		C_2H_5OH	10.4 (1.26)	16.7 (1.37)
		$CHCl_3$	10.8 (0)	17.5 (1.7)*
	$CH_2CH_2CH_2OCH_3$	solid	16.1	
		$CHCl_3$	16.0 (1.90)	
		pyridine	10.1 (1.09)	17.2 (1.12)

ν: 10^3 cm^{-1}. * shoulder.

It was shown formerly that $Ni(Sal.CH_2CH_2OCH_3)_2$ is square-planar in non-donor solvents and in the solid state, the OCH_3-group being unbound to the nickel(II) ion, although the complexes of the $Ni(Sal.CH(R)CH_2OCH_3)_2$ type have a hexacoordinated, octahedral configuration with the OCH_3-group bound to the nickel(II) ion.6) The difference in the coordination around the nickel(II) ion between $Ni(X\text{-}Sal.CH_2CH_2OH)_2$ and $Ni(Sal.CH_2CH_2OCH_3)_2$ may be in agreement with the current view that the OH-group has a higher tendency to combine with the metal ion than has the OCH_3-group.

In a similar way, it is concluded from the electronic absorption spectrum that $Ni(Sal.CH_2CH(CH_3)OH)_2$ and $Ni(3\text{-}CH_3O\cdot SalCH_2CH(CH_3)OH)_2$ take an octahedral configuration in the solid state and in non-donor solvents, the fifth and the sixth coordination position around the nickel(II) being occupied by the two OH-groups (Fig. 4). The reflectance spectra of the complexes in the solid state, however, show *d-d* absorption bands at slightly lower frequencies than do the spectra of the complexes in non-donor solvents. It is likely that the distortion from the regular octahedral configuration is greater for the solid state than for solution in non-donor solvents.

For $R=C(CH_3)_2CH_2OH$, the steric condition around the nickel(II) ion is much congested. The present work reveals that for $R=C(CH_3)_2CH_2OH$

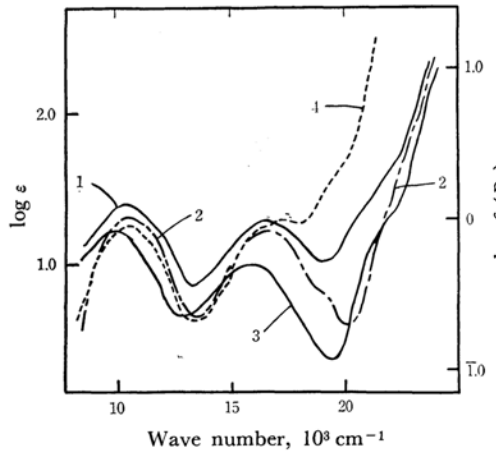

Fig. 4. Electronic absorption spectra of $Ni(3\text{-}CH_3O\text{-}Sal.R)_2$: 1, $R=CH_2CH(CH_3)OH$, in the solid state (by reflectance); 2, $R=CH_2CH(CH_3)OH$, in ethanol; 3, $R=C(CH_3)_2CH_2OH$, in the solid state (by reflectance); 4, $R=C(CH_3)_2CH_2OH$, in methanol.

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6) A. Chakravorty, J. P. Fennessey and R. H. Holm, *Inorg. Chem.*, **4**, 26 (1965).

and X=H and 3-CH_3O, the nickel(II) complexes in the solid state, in methanol or in ethanol at room temperature show absorption spectra typical of the hexa-coordinated nickel(II) complex (Fig. 4). This result is very interesting, since the previous work showed that, for R=*t*-C_4H_9 and X=H, the steric hindrance due to the bulky *t*-C_4H_9 group made it quite difficult for the nickel(II) complex to take a square-planar configuration, the tetrahedral configuration only being allowed.[1,7)]

For Ni(Sal.C$(CH_3)_2CH_2OH)_2$, the configuration of the complex in chloroform is different from that in the methanol solution, as is inferred from the difference in the color of the solution between the two; the chloroform solution is red and the methanol solution is green. The chloroform solution shows absorption band at about 10.7×10^3 cm^{-1} (log ε nearly 0) and much more intense absorption in the higher frequency region, the latter being superposed almost totally by the stronger absorption due mainly to the ligand groups (Fig. 5). Thus the spectrum of the chloroform solution is different from any of the spectra of the tetrahedral, the octahedral and the penta-coordinated complex of nickel(II), but similar to the spectrum typical of the square-planar nickel(II) complex. It is likely that the complex in chloroform exists predominantly as a square-planar complex. The occurrence of the square-planar configuration for this complex in chloroform is remarkable, particularly in view of the fact that Ni(Sal.*t*-$C_4H_9)_2$ takes a tetrahedral configuration due to the steric hindrance.[1)] The reason for this is not completely clarified at the moment, but the OH-group probably plays a part in this phenomenon.

In a similar way, the inspection of the electronic spectrum (Table 2) shows that Ni(Sal.C$(CH_3)_2$-$CH_2OH)_2$ in pyridine is different from that of the tetrahedral or the square-planar nickel(II) complex.

The final answer about the structure of the nickel(II) complex in pyridine, however, should be drawn after more extensive studies.

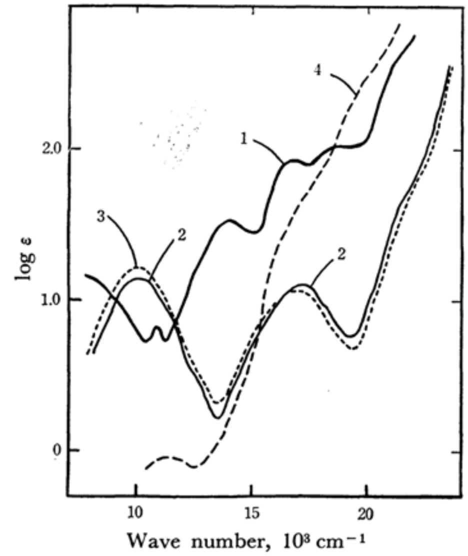

Fig. 5. Electronic absorption spectra of Ni(X-Sal.-R$)_2$; 1, R=C$(CH_3)_3$ and X=H, in pyridine; 2, R=CH$(CH_3)_2$ and X=H, in pyridine; 3, R=cyclohexyl and X=H, in pyridine; 4, R=C$(CH_3)_2CH_2OH$ and X=3-CH_3O, in chloroform.

The electronic absorption spectrum also shows clearly that Ni(Sal.*t*-$C_4H_9)_2$ is tetrahedral even in pyridine. It is again to be noted that the result for the complex with R=C$(CH_3)_2CH_2OH$ is different from the result for the complex with R=*t*-C_4H_9. As mentioned above, the difference in this respect between C$(CH_3)_2CH_2OH$ and *t*-C_4H_9 may be due possibly to the presence of the OH-group in the former, but the detailed explanation may not be feasible for the present. In connection with this, it is worth noting that Ni(Sal.-*iso*-$C_3H_7)_2$ and Ni(Sal.cyclohexyl$)_2$ in pyridine are hexa-coordinated with two pyridine molecules bound to the nickel(II) ion (Table 2).

The present authors are grateful to the Ministry of Education for financial support.

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7) L. Sacconi, "Essays in Coordination Chemistry," ed. by W. Schneider, G. Anderegg and R. Gut, Birkhauser Verlag, Basel (1964), p. 148.