April, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 1083—1085 (1982) 1083

Stereochemistry of Bis[*N*-(2,6-diisopropylphenyl)salicylideneaminato]copper(II) and nickel(II) Complexes

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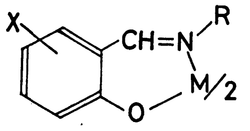
(Received October 3, 1981)

Bis[*N*-(2,6-diisopropylphenyl)salicylideneaminato]copper(II) and nickel(II) complexes have been synthesized. Their configurations in the solid state, in chloroform, and in pyridine have been examined and discussed in comparison with those of the related complexes.



The stereochemistry of copper(II) and nickel(II) complexes with bidentate *N*-arylsalicylideneaminates (I, abbreviated as $M(X\text{-sal-}R)_2$) has been extensively studied.[1,2] For the most part, the copper(II) complexes of this series are planar, while the nickel(II) complexes are planar or multinuclear.[3] Bis[*N*-(2,6-dialkylphenyl)-salicylideneaminato]copper(II) and nickel(II) complexes, the alkyl being methyl or ethyl, were examined previously, with the view of investigating the effects of the substituents at the 2- and 6-positions of the salicylidene moiety on the structure of the metal complexes.[2–5] According to previous data on crystal structure analyses, the phenyl group is expected to be essentially perpendicular to the salicylideneaminate plane.[1] It also seems to be significant to examine the corresponding complexes with 2,6-diisopropylphenyl, the isopropyl being evidently more bulky than methyl and ethyl. Examination of bis[*N*-(2,6-diisopropylphenyl)-salicylideneaminato]cobalt(II) complexes, abbreviated as $Co(X\text{-sal-dpp})_2$, revealed that the planar structure was neither precluded nor destabilized, but some of the cobalt(II) complexes (X=5-Br and 5-Cl) were forced into the planar structure in the solid state.[5] A similar study has now been extended to the copper(II) and nickel(II) complexes with the same ligands. The present paper describes the accounts of the study.

Experimental

Materials. 2,6-Diisopropylaniline was obtained commercially. Bis[*N*-(2,6-diisopropylphenyl)salicylideneaminato]-copper(II) and nickel(II) and analogous species, which are abbreviated as $M(X\text{-sal-dpp})_2$, were synthesized in the same way as reported previously.[3] They are readily soluble in chloroform, benzene, and acetone, but sparingly soluble in ethanol. The nickel(II) complexes are olive-green, while the copper(II) complexes are brown-olive. Monopyridine adducts of the copper(II) complexes were obtained in dark green crystals by the addition of water or hexane to the pyridine solutions of the parent complexes. Analytical data of these complexes are given in Table 1.

Measurements. Electronic absorption spectra of the complexes in solution and in Nujol were recorded on a Shimadzu MPS-500 spectrophotometer. Magnetic measurements at room temperature were carried out by the Gouy method using $CoHg(SCN)_4$ as a calibrant.

Results and Discussion

Copper(II) Complexes. Bis(*N*-arylsalicylideneaminato)copper(II) complexes (I, R=Ph, $Y\text{-}C_6H_4$) normally prefer the planar geometry.[1–3] Electronic absorption spectra of $Cu(X\text{-sal-dpp})_2$ (X=H, 5-Br, 5-NO_2, and 3-CH_3O) in chloroform and in Nujol (Fig. 1) are remarkably similar to each other and bear a close resemblance to the spectra of the copper(II)

Table 1. Analytical data of bis[*N*-(2,6-diisopropylphenyl)salicylideneaminato]-copper(II) and nickel(II) and their monopyridine adducts

Compound	Calcd(%)			Found (%)			μ/BM
	H	C	N	H	C	N	
$Cu(H\text{-sal-dpp})_2$	7.10	73.11	4.49	7.17	73.03	4.55	1.9
$Cu(H\text{-sal-dpp})_2\cdot py$	7.02	73.42	5.97	7.01	73.13	5.94	2.1
$Cu(5\text{-Br-sal-dpp})_2$	5.41	58.35	3.58	5.56	58.22	3.51	1.9
$Cu(5\text{-Br-sal-dpp})_2\cdot py$	5.50	59.97	4.88	5.40	59.83	4.94	2.0
$Cu(5\text{-}NO_2\text{-sal-dpp})_2$	5.93	63.89	7.84	5.83	64.28	7.77	1.8
$Cu(5\text{-}NO_2\text{-sal-dpp})_2\cdot py$	5.97	65.09	8.83	6.09	65.40	9.20	2.0
$Cu(3\text{-}CH_3O\text{-sal-dpp})_2$	7.07	70.20	4.09	6.87	70.41	4.17	1.8
$Cu(3\text{-}CH_3O\text{-sal-dpp})_2\cdot py$	6.98	70.81	5.51	7.12	70.75	5.56	2.0
$Ni(H\text{-sal-dpp})_2$	7.16	73.68	4.52	7.24	73.54	4.56	dia
$Ni(5\text{-Br-sal-dpp})_2$	5.45	58.72	3.60	5.56	58.84	3.50	dia
$Ni(5\text{-Cl-sal-dpp})_2$	6.15	66.30	4.07	6.10	66.48	4.15	dia
$Ni(5\text{-}NO_2\text{-sal-dpp})_2$	5.97	64.33	7.90	5.98	64.25	7.91	dia
$Ni(3\text{-}CH_3O\text{-sal-dpp})_2$	7.12	70.70	4.12	7.36	70.98	4.15	dia

μ: BM at room temperature. dia: Diamagnetic. py: Pyridine.

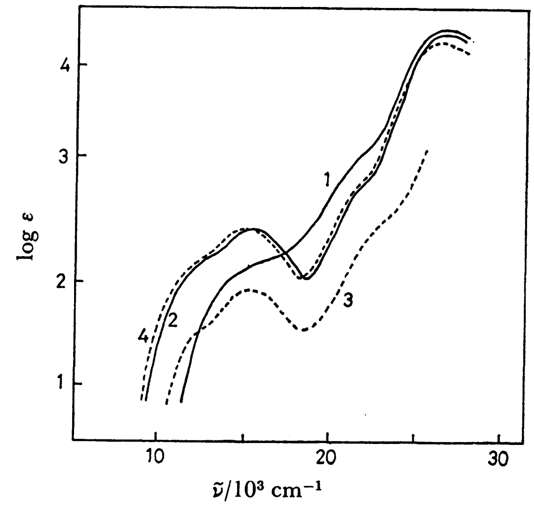


Fig. 1. Electronic absorption spectra of copper(II) complexes: 1, Cu(H-sal-dpp)$_2$ in CHCl$_3$; 2, Cu(H-sal-dpp)$_2$ in pyridine; 3, Cu(H-sal-dpp)$_2$-py in Nujol; 4, Cu(H-sal-2,6-Et$_2$-C$_6$H$_3$)$_2$ in pyridine.

complexes (I, R=Ph, 2,6-Me$_2$-C$_6$H$_3$, and 2,6-Et$_2$-C$_6$H$_3$), which were previously concluded to be planar.[2,3] Some of the representative spectra are shown in Fig. 1. It is thus presumed that the complexes Cu(X-sal-dpp)$_2$ are planar in the solid state and in chloroform.

The spectra of Cu(X-sal-dpp)$_2$ in pyridine have a d-d band maximum at 15.3 × 10^3 cm^{-1} with a shoulder on the lower frequency side. They are strikingly similar to each other, irrespective of the substituent X, showing that all these copper(II) complexes have essentially the same geometry. The spectra obey Beer's law in pyridine as well as in chloroform and are also remarkably similar to those of the complexes (I, R=Ph, 2,6-Et$_2$-C$_6$H$_3$), as shown in Fig. 1.[3] It is thus presumed that all these copper(II) complexes in pyridine exist exclusively as penta-coordinate monopyridine adducts. The monopyridine addusts can also be isolated in crystals from the pyridine solutions of the parent complexes. Electronic spectra of the monopyridine adducts in Nujol are similar to those of the parent complexes in pyridine (Fig. 1).

Nickel(II) Complexes. The complexes Ni(X-sal-dpp)$_2$ (X=H, 5-Cl, 5-Br, 5-NO$_2$, and 3-CH$_3$O) are all diamagnetic and consist of tetra-coordinate planar complexes in the solid state. Their spectra in chloroform and in Nujol are typical of the spin-paired, planar nickel(II) complexes with a d-d band at about 16—17 × 10^3 cm^{-1}. Representative spectra are shown in Fig. 2 and the maxima of the d-d bands are set out in Table 2. It is thus found that the steric condition in these complexes does not exclude the planar geometry. In this connection, it is interesting to remark that the complexes Co(X-sal-dpp)$_2$ (X=5-Br and 5-Cl) in the solid state prefer the planar geometry to the tetrahedral one, which is normally adopted by the tetra-coordinate

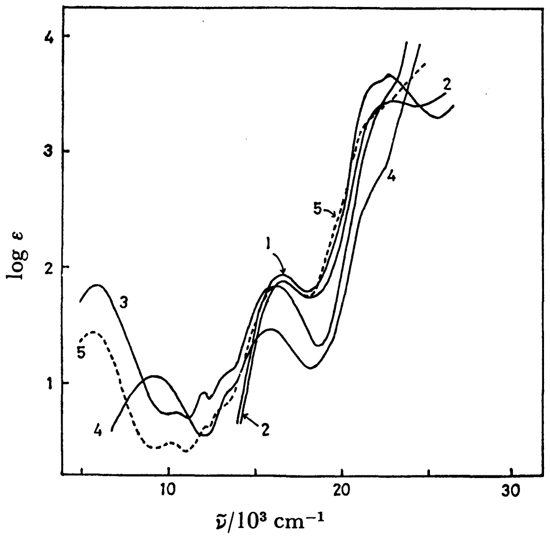


Fig. 2. Electronic absorption spectra nickel(II) complexes: 1, Ni(H-sal-dpp)$_2$ in CHCl$_3$; 2, Ni(H-sal-dpp)$_2$ in pyridine; 3, Ni(5-NO$_2$-sal-dpp)$_2$ in pyridine; 4, Ni(3-CH$_3$O-sal-dpp)$_2$ in pyridine; 5, Ni(5-Cl-sal-dpp)$_2$ in pyridine.

TABLE 2. ABSORPTION MAXIMA OF d-d BANDS OF BIS[*N*-(2,6-DIISOPROPYLPHENYL)-SALICYLIDENEAMINATO]NICKEL(II), Ni(X-sal-dpp)$_2$

Compound	Medium	$\tilde{\nu}/10^3$ cm^{-1} (log ε)
Ni(H-sal-dpp)$_2$	CHCl$_3$	16.6(1.92)
	Nujol	16.6
	Pyridine	16.5(1.87)
Ni(5-Cl-sal-dpp)$_2$	CHCl$_3$	16.5(2.02)
	Nujol	16.5
	Pyridine	5.5(1.44), 16.5(1.88)
Ni(5-Br-sal-dpp)$_2$	CHCl$_3$	16.4(1.98)
	Nujol	16.5
	Pyridine	5.4(1.56), 16.3(1.84)
Ni(5-NO$_2$-sal-dpp)$_2$	CHCl$_3$	17.2(2.16)
	Nujol	17.1
	Pyridine	5.8(1.85), 16.1(1.82)
Ni(3-CH$_3$O-sal-dpp)$_2$	CHCl$_3$	16.1(1.96)
	Nujol	16.1
	Pyridine	9.1(1.06), 15.8(1.47)

cobalt(II) complexes.[5]

The d-d band maxima ($\tilde{\nu}$) of the planar nickel(II) complexes Ni(X-sal-dpp)$_2$ decrease in the following order as to the substituent X: 5-NO$_2$>H>5-Cl≈5-Br>3-CH$_3$O (series 1).

The present study indicates that it depends upon X whether or not and to what extent the complexes Ni(X-sal-dpp)$_2$ bind additional pyridine molecules, when dissolved in pyridine. The complex Ni(H-sal-dpp)$_2$ in pyridine exists mostly as the planar species, the penta-coordinate or hexa-coordinate pyridine adducts hardly being detected. The spectrum of the pyridine solution differs very little from that of the chloroform solution (Fig. 2).

On the contrary, Ni(3-CH$_3$O-sal-dpp)$_2$ in pyridine exists exclusively as hexa-coordinate species. The spectra have d-d bands at 9.4 and 15.9×10^3 cm^{-1} (Table 2), no absorption being observed at about 5—6×10^3 cm^{-1} (expected for the penta-coordinated species) or at about 16—17×10^3 cm^{-1} (for the tetra-coordinate species).

The complex Ni(5-NO$_2$-sal-dpp)$_2$ in pyridine exists entirely as penta-coordinate species. The spectrum is strikingly similar to that of the penta-coordinate nickel(II) complex.[4] Beer's law is found to hold, so that the assumption of equilibria involving various species with different structures is not required.

TABLE 3. STRUCTURES OF BIS[*N*-(2,6-DIALKYLPHENYL)-SALICYLIDENEAMINATO]NICKEL(II) COMPLEXES Ni(X-sal-R)$_2$ IN PYRIDINE[a)

X	R		
	2,6-Me$_2$-C$_6$H$_3$$^{b)}$	2,6-Et$_2$-C$_6$H$_3$$^{b)}$	2,6-(*i*-Pr)$_2$-C$_6$H$_3$
5-NO$_2$	6	6	5
H	4(65)+5(35)	4(80)+5(20)	4(95)+5(5)
5-Cl	4(20)+5(80)	4(40)+5(60)	4(70)+5(30)
5-Br	4(20)+5(80)	4(50)+5(50)	4(70)+5(30)
3-CH$_3$O	6	6	6

a) These nickel(II) complexes are tetra-coordinate-planar in non-donor solvents and in the solid state. The numbers in the parentheses are approximate proportions in percentage of the species in the solutions. The numbers of one figure in the table denote the coordination numbers. See also the text. b) The data are taken from Refs. 3 and 4 in the text.

The complexes Ni(5-Br-sal-dpp)$_2$ and Ni(5-Cl-sal-dpp)$_2$ in pyridine exist as equilibrium mixtures of the tetra-coordinate planar and penta-coordinate species. The spectra have a d-d band characteristic of the planar species at about 16.5×10^3 cm^{-1} and another d-d band characteristic of the penta-coordinate species at about 5.5×10^3 cm^{-1}, no absorption being observed at about 9—10×10^3 cm^{-1}, where the hexa-coordinate species is expected to absorb. McKenzie and coworkers made some approximate but useful estimates of the relative amounts of the species present in the solutions of the nickel(II) complexes (I, R=2,6-Me$_2$-C$_6$H$_3$ and 2,6-Et$_2$–C$_6$H$_3$) on the basis of the intensities of the various d-d bands in the spectra of these nickel(II) complexes.[4] Similar estimates have been made for the present nickel(II) complexes, following the method of McKenzie. The results of the estimates are shown in Table 3, the relevant data on the related complexes being included for comparison.[3,4] Numbers of one figure in the table represent the coordination numbers at the nickel(II) ion. The number 4 denotes "planar tetra-coordination."

Inspection of Table 3 indicates that the order as to the ability of Ni(X-sal-dpp)$_2$ to bind additional ligands is found to be lower than that of the corresponding dimethylphenyl and diethylphenyl complexes, showing that the steric effect of 2,6-diisopropylphenyl is larger than that of the 2,6-dimethyl- or 2,6-diethylphenyl. For instance, the difference in this respect is apparently noticed in the complexes with X=5-NO$_2$. Attempts to isolate penta-coordinate pyridine adducts Ni(X-sal-dpp)$_2$·py have not been successful so far, whereas the penta- and hexa-coordinate pyridine adducts of the 2,6-dimethylphenyl and 2,6-diethylphenyl complexes were isolated in crystals.[4]

Inspection of Table 3 also indicates that higher coordination numbers are favored in the following order as to X: 3-CH$_3$O>5-NO$_2$>5-Br≈5-Cl>H. The order, which is not in agreement with the series (1), results from the total effects of such factors as bulk steric effects, the electron-withdrawing power of the ring substituent, and the ligand-field strength of the salicylideneaminates. At the moment, however, there seems to be no unambiguous explanation for the order.

Financial support of this work by the Ministry of Education is gratefully acknowledged.

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