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Nickel(II) and Copper(II) Complexes of *C,N*-Disubstituted Salicylideneimines with Steric Hindrance

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Many new nickel(II) and copper(II) complexes (abbreviated as M(X-sal.R)$_2$) of Schiff bases were obtained from *C*-substituted salicylaldehydes and 2,6-dimethyl- and 2,6-diethyl-aniline, where X denotes 5-Br, 5-Cl, 5,6-benzo, 5-NO$_2$ and 3-CH$_3$O. For X = 5-Cl, the corresponding nickel(II) complex with R = 2,6-dichlorophenyl was also synthesized. All these nickel(II) complexes consist of square-planar molecules in the solid state and in non-donor solvents. The nickel(II) complexes, when dissolved in pyridine, either take up two pyridine molecules to form six-coordinated complexes or retain the original planar configuration. The configuration in pyridine depends upon the nature of X, demonstrating that the effect of X on the electronic state of the ligand may also be important, besides the steric factor, in determining the configuration of the nickel(II) complexes. The corresponding copper(II) complexes, which are square-planar in the solid state and in non-donor solvents, combine with one or two pyridine molecules, when dissolved in pyridine.

Numerous papers have been published about nickel(II) and copper(II) complexes of Schiff bases obtained from *C*-substituted salicylaldehydes (Fig. 1).[*1] It is expected, however, that a com-

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[*1] These metal complexes are abbreviated as M(X-sal.R)$_2$ in this paper.

plication may occur with these complexes, when steric hindrance is considerable. For R=2,6-$(CH_3)_2$Ph and 2,6-$(C_2H_5)_2$Ph,*[2] for example, where steric hindrance is large, complexes of the Ni(X-sal.R)$_2$ type are known to behave differently from the complexes of a similar type with R=phenyl or monosubstituted phenyl showing little or no steric hindrance.[1-3] The behavior of these complexes may also depend upon the nature of X, since the electronic state of the oxygen and the nitrogen atom of these ligands, X-sal.R, may be expected to change in a delicate way on changing X. In order to see the possible effect of the substituent X on the stereochemistry of the metal complexes and to explore a possibility of finding 5-coordinated complexes, the nickel(II) complexes of the Ni(X-sal.R)$_2$ type have been synthesized in the present work with 2,6-$(CH_3)_2$Ph and 2,6-$(C_2H_5)_2$Ph for R. A similar study has also been carried out about the corresponding copper(II) complexes for comparison with the nickel(II) complexes.

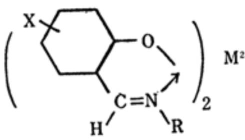

Fig. 1. M(X-sal.R)$_2$.

Experimental

Materials. Bis(*N*-aryl-*C*-substituted salicylideneiminato)nickel(II) complexes were prepared by a method similar to that previously reported either by reaction of a bis(*C*-substituted salicylaldehydato)nickel(II) with an amine or by reaction of nickel(II) acetate with a mixture of a *C*-substituted salicylaldehyde and an amine.[1,4] Pure crystals of the compounds were obtained by recrystallization of crude product using suitable organic solvents like ethanol, acetone and ethyl ether. Elemental analyses of the new nickel(II) compounds are given in Table 1. They are all green.

Bis(*N*-aryl-*C*-substituted salicylideneiminato)copper(II) complexes were also prepared by a method similar to that previously reported.[1,2,4] Purification of the complexes was carried out by recrystallization of crude product from suitable organic solvents like ethanol, chloroform and ethyl ether. Elemental analyses of the new copper(II) complexes are given in Table 2.

Measurements. The electronic absorption spectra of the metal complexes in solution and reflection spectra of the solid were determined with a Shimadzu QR-50 spectrophotometer and a Shimadzu MPS-50L spectrophotometer. Pyridine for a solvent was purified, whenever necessary, by distillation after having been dried with potassium carbonate.

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

Results and Discussion

The Nickel(II) Complexes of *N*-Aryl-*C*-Substituted Salicylideneimines. Many new nickel(II) complexes of the Ni(X-sal.R)$_2$ type have been prepared in the present work (Table 1). The result that all these nickel(II) complexes are diamagnetic in the solid state indicates the planar configuration of these complexes. They afford examples of the green nickel(II) complexes which are diamagnetic and planar.

Table 1. Analytical data of nickel(II) complexes of the Ni(X-sal.R)$_2$ type

X	R*	Calcd, %			Found, %		
		C	H	N	C	H	N
5-Cl	$(CH_3)_2$Ph	62.54	4.55	4.86	62.49	4.79	4.87
	$(C_2H_5)_2$Ph	64.59	5.42	4.43	64.25	5.52	4.56
	Cl_2Ph	47.47	2.14	4.26	47.75	1.81	4.30
5-Br	$(CH_3)_2$Ph	54.18	3.94	4.21	54.47	3.80	4.25
	$(C_2H_5)_2$Ph	56.61	4.75	3.88	56.77	4.51	3.80
5,6-Benzo	$(CH_3)_2$Ph	74.89	5.62	4.60	75.57	5.21	4.67
	$(C_2H_5)_2$Ph	75.79	6.36	4.21	75.93	6.02	4.24
3-CH_3O	$(CH_3)_2$Ph	67.75	5.68	4.94	67.50	5.56	4.86
	$(C_2H_5)Ph_2$	69.36	6.47	4.49	69.10	6.43	4.55
5-NO_2	$(CH_3)_2$Ph	60.33	4.39	9.38	60.19	4.11	9.71
	$(C_2H_5)_2$Ph	62.50	5.25	8.58	61.43	5.07	8.98

* 2,6-disubstituted phenyl groups

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*[2] The notation Ph denotes a benzene nucleus.

1) S. Yamada, *Coordin. Chem. Reviews*, **1**, 415 (1966).

2) S. Yamada, H. Nishikawa and E. Yoshida, This Bulletin, **39**, 994 (1966).

3) S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi and K. Iwasaki, *Coordin. Chem. Reviews*, **3**, 247 (1968).

4) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, "Progress in Inorganic Chemistry," Vol. VII, ed. by F. A. Cotton, Interscience Publishers, New York, N. Y. (1966), p. 83.

TABLE 2. ANALYTICAL DATA OF COPPER(II) COMPLEXES OF THE $Cu(X\text{-}sal.R)_2$ TYPE

X	R*	Calcd, %			Found, %		
		C	H	N	C	H	N
5-Cl	$(CH_3)_2Ph$	62.02	4.51	4.82	61.99	4.36	4.93
	$(C_2H_5)_2Ph$	64.09	5.38	4.40	63.65	5.28	4.44
5,6-Benzo	$(CH_3)_2Ph$	74.55	5.27	4.58	73.68	5.00	4.52
	$(CH_3)_2Ph$**				74.20	5.12	4.63
	$(C_2H_5)_2Ph$	75.48	6.03	4.19	75.27	6.11	4.20
$3\text{-}CH_3O$	$(CH_3)_2Ph$	67.18	5.64	4.90	67.09	5.71	5.02
	$(CH_3)_2Ph$**				67.25	5.72	5.14
	$(C_2H_5)_2Ph$	68.82	6.42	4.46	68.54	6.52	4.28
$5\text{-}NO_2$	$(CH_3)_2Ph$	59.84	4.35	9.31	59.90	4.72	8.96
	$(C_2H_5)_2Ph$	62.04	5.21	8.51	60.99	4.99	8.38

* 2,6-disubstituted phenyl groups, unless otherwise indicated.
** 2,5-disubstituted phenyl groups.

It is well known that the electronic spectrum of a nickel(II) complex varies remarkably according as the nickel(II) complex is square-planar, tetrahedral, five-coordinated, or octahedral.[1-3] The present work shows that the electronic spectra of $Ni(X\text{-}sal.2,6\text{-}(CH_3)_2Ph)_2$ and $Ni(X\text{-}sal.2,6\text{-})C_2H_5)_2\text{-}Ph)_2$ in non-donor solvents are typical of the square-planar nickel(II) complex (Fig. 2 and Table 3), and similar to the spectra of $Ni(H\text{-}sal.2,6\text{-}(CH_3)_2Ph)_2$ and $Ni(H\text{-}sal.2,6\text{-}(C_2H_5)_2Ph)_2$, which were previously concluded to be square-planar.[2] These complexes show no absorption band at about 900—1000 mμ, where the tetrahedral or the octahedral nickel(II) complexes are expected to absorb. Hence, both the presence of the monomeric, tetrahedral species and the association of the square-planar complexes may be excluded near room temperature. It is known[6,7] that bis(*N*-monosubstituted phenylsalicylideneiminato)nickel(II) complexes in non-donor solvents consist of the square-planar monomer, the associated polymer with the six-coordinated nickel(II), and the tetrahedral monomer, the former two being in equilibrium with each other near room temperature. The difference in this respect between the *N*-monosubstituted phenyl- and the *N*-2,6-disub-

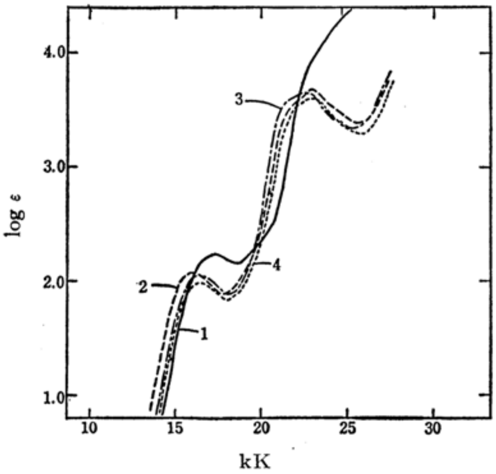

Fig. 2. Electronic absorption spectra of $(NiX\text{-}sal.\text{-}2,6\text{-}Y_2Ph)_2$ in chloroform.
1, $X=5\text{-}NO_2$, $Y=CH_3$; 2, $X=3\text{-}CH_3O$, $Y=CH_3$;
3, $X=5\text{-}Cl$, $Y=C_2H_5$; 4, $X=H$, $Y=C_2H_5$

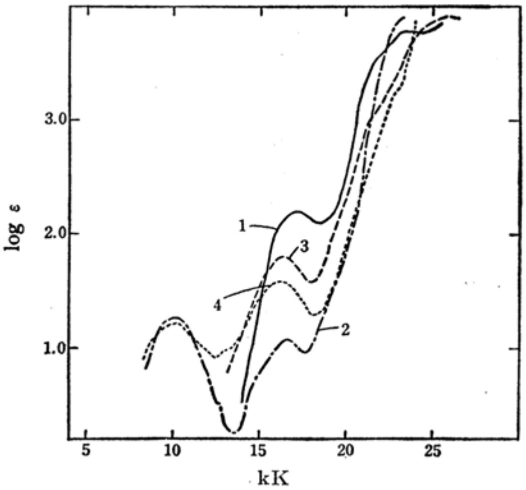

Fig. 3. Electronic absorption spectra of $Ni(X\text{-}sal.\text{-}2,6\text{-}Y_2Ph)_2$ in pyridine.
1, $X=5,6\text{-benzo}$, $Y=CH_3$; 2, $X=5\text{-}Cl$, $Y=CH_3$;
3, $X=5\text{-}Br$, $Y=CH_3$; 4, $X=5\text{-}NO_2$, $Y=CH_3$

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5) S. Yamada and H. Nishikawa, This Bulletin, **36**, 755 (1963).

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

7) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).

stituted phenyl-salicylideneiminato-nickel(II) complexes was ascribed mainly to the steric condition.[2)] The same explanation applies to Ni(X-sal.2,6-$(CH_3)_2$Ph$)_2$ and Ni(X-sal.2,6-$(C_2H_5)_2$Ph$)_2$, which have been concluded to be square-planar in the solid state and in non-donor solvents.

The configuration of these nickel(II) complexes in pyridine, however, remarkably depends upon the substituent X. Electronic absorption spectra (Fig. 3 and Table 3) clearly show that, for X=5,6-benzo and 5-Br and R=2,6-$(CH_3)_2$Ph and 2,6-$(C_2H_5)_2$Ph, the complexes of the Ni(X-sal.R$)_2$ type bind no additional pyridine molecule, the original square-planar configuration being retained in pyridine. This result, which is the same as that for X=H, is considered to be due mainly to the steric hindrance arising from the two alkyl groups.

TABLE 3. ABSORPTION MAXIMA OF NICKEL(II) COMPLEXES OF THE Ni(X-sal.R$)_2$ TYPE*

X	Y	Solvent	ν**	log ε
5-Br	CH_3	$CHCl_3$	16.6	2.07
		Pyridine	16.3	1.80
	C_2H_5	CH_2Cl_2	16.4	2.04
		Pyridine	16.7	1.84
5-Cl	CH_3	CH_2Cl_2	16.1	2.08
		Pyridine	10.1	1.26
			16.6	1.08
	C_2H_5	$CHCl_3$	16.3	2.05
		Pyridine	16.2	1.84
	Cl	$CHCl_3$	16.0	2.04
		Pyridine	10.0	1.00
			16.2	1.55
5,6-Benzo	CH_3	$CHCl_3$	16.9	2.26
		Pyridine	17.1	2.20
	C_2H_5	$CHCl_3$	16.9	2.21
		Pyridine	17.1	2.22
5-NO_2	CH_3	$CHCl_3$	17.2	2.23
		Pyridine	10.1	1.13
			16.2	1.50
	C_2H_5	$CHCl_3$	17.1	2.25
		Pyridine	9.9	1.20
			16.1	1.58
3-CH_3O	CH_3	$CHCl_3$	16.0	2.07
		Pyridine	9.4	1.10
			15.9	1.40
	C_2H_5	$CHCl_3$	16.0	2.03
		Pyridine	9.5	1.06
			15.9	1.38

* R=2,6-Y_2Ph ** ν, 10^3 cm^{-1}

It is found from the spectra (Fig. 3 and Table 3) that for X=5-NO_2 and 3-CH_3O, the complexes of the Ni(X-sal.2,6-$(CH_3)_2$Ph$)_2$ and Ni(X-sal.2,6-$(C_2H_5)_2$Ph$)_2$ type, when dissolved in pyridine, exist as the six-coordinated pyridine solvates of the Ni(X-sal.2,6-Y_2Ph$)_2$(py$)_2$ type,[*3] which show electronic spectra typical of octahedral, six-coordinated nickel(II) complexes. The absorption maxima of these pyridine solvates at about 10 and 16 kK may be assigned as $^3T_{2g}\leftarrow{}^3A_{2g}$ and $^3T_{1g}$-(F)$\leftarrow{}^3A_{2g}$ in the scheme of the O_h ligand field symmetry.

Since Beer's law was obeyed, no equilibrium between the octahedral complex and another species may be likely. This difference between the two types of the substituent for X, which is not considered to be due to the steric factor, indicates that, although steric hindrance in these nickel(II) complexes seems to be more or less effective, it does not absolutely exclude the coordination number exceeding four. This result may be interpreted in terms of the difference in the electronic factor due to various X groups.

For X=5-Cl, anomalous behavior was observed. For example, the Ni(X-sal.2,6-$(CH_3)_2$Ph$)_2$ in pyridine exists as a six-coordinated complex, Ni(X-sal.R$)_2$(py$)_2$, as clearly seen from the electronic spectrum (Fig. 3 and Table 3). On the contrary, Ni(5-Cl.sal.2,6-$(C_2H_5)_2$Ph$)_2$ in pyridine retains the planar configuration. The difference between the complexes with X=5-Cl and with X=5-Br on one hand and between the complexes with R=2,6-$(CH_3)_2$Ph and with R=2,6-$(C_2H_5)_2$Ph for X=5-Cl on the other may also be due to the electronic factor. This fact seems to be in agreement with the fact that the band maximum and consequently the ligand field strength for X=5-Cl and R=2,6-$(CH_3)_2$Ph is slightly lower than the maximum for X=5-Cl and R=2,6-$(C_2H_5)_2$Ph.

It is significant that there is a remarkable difference between the two types of substituents for X. One includes 5-Br and 5,6-benzo, in addition to X=H, and the other 5-NO_2 and 3-CH_3O. The

TABLE 4. CONFIGURATION OF NICKEL(II) COMPLEXES OF THE Ni(X-sal.2,6-Y_2Ph$)_2$ TYPE IN PYRIDINE

X	Y	Config. in pyridine
H	CH_3	four-coordinated (original)
	C_2H_5	four-coordinated (original)
5-Br	CH_3	four-coordinated (original)
	C_2H_5	four-coordinated (original)
5-Cl	CH_3	six-coordinated solvate
	C_2H_5	four-coordinated (original)
	Cl	six-coordinated solvate
5,6-Benzo	CH_3	four-coordinated (original)
	C_2H_5	four-coordinated (original)
5-NO_2	CH_3	six-coordinated solvate
	C_2H_5	six-coordinated solvate
3-CH_3O	CH_3	six-coordinated solvate
	C_2H_5	six-coordinated solvate

[*3] The notation py denotes a pyridine molecule.

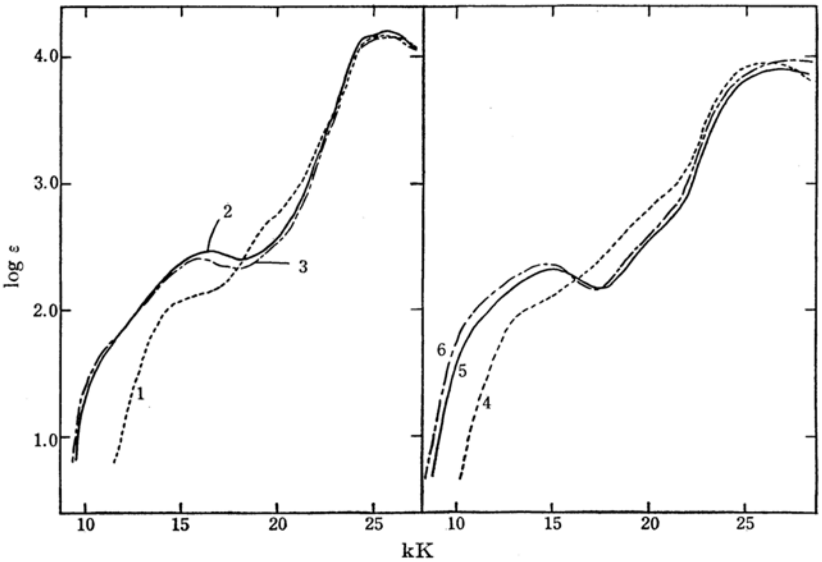

Fig. 4. Electronic absorption spectra of $Cu(X\text{-}sal.2,6\text{-}Y_2Ph)_2$ in solution.
1, X=5,6-benzo, $Y=CH_3$, in chloroform; 2, X=5,6-benzo, $Y=CH_3$, in pyridine;
3, X=5,6-benzo, $Y=C_2H_5$, in pyridine; 4, $X=3\text{-}CH_3O$, $Y=CH_3$, in chloroform;
5, $X=3\text{-}CH_3O$, $Y=CH_3$, in pyridine; 6, $X=3\text{-}CH_3O$, $Y=C_2H_5$, in pyridine

result of the examination in this work about the configuration of these nickel(II) complexes in pyridine is summarized in Table 4.

In the case of the corresponding cobalt(II) complexes, five-coordinated pyridine solvates of the $Co(X\text{-}sal.2,6\text{-}Y_2Ph)_2(py)$ type were often formed.[8,9] Comparison of the results in the present work with that of the cobalt(II) complexes shows that the stability of the five-coordinated species *vis-a-vis* the four- and the six-coordinated ones is lower for the nickel(II) complexes than for the cobalt(II) complexes.

The Copper(II) Complexes of *N*-Aryl-*C*-substitutued Salicylideneimines. Many new copper(II) complexes of the *C*-substituted salicylideneimines, which are shown in Table 2, have been prepared in the present work. The planar configuration is most likely for these copper(II) complexes, since the tendency of the copper(II) complexes to take the square-planar configuration is known to be very high for the ligands of this series. The square-planar configuration may also be most likely even for 2,6-disubstituted phenyl derivatives in spite of the steric condition, since the corresponding nickel(II) complexes as well as the corresponding copper(II) complexes of salicylideneimines[2] have also been found to be square-planar. This presumption is supported by the present finding that the complexes of the $Cu(X\text{-}sal.2,6\text{-}Y_2Ph)_2$ type show ligand field bands at frequencies nearly identical with those of $Cu(X\text{-}sal.YPh)_2$, which were previously concluded to be planar.[2] It was also concluded previously that the ligand field band was shifted toward a considerably lower frequency when the copper(II) complex was distorted appreciably from the square-planar configuration.[4,6]

The spectral change in the ligand field band region of these copper(II) complexes on going from a non-donor solvent to pyridine (Figs. 4 and 5) is similar to the change observed previously when the four-coordinated complex of copper(II) takes up one or two additional ligands to form a five- or a six-coordinated complex.[2,10] It may be concluded, therefore, that all the copper(II) complexes examined in the present work combine with one or two pyridine molecules in the pyridine solution. This result is the same as the previous conclusion[2] with $Cu(H\text{-}sal.2,6\text{-}Y_2Ph)_2$, Y_2 being $(CH_3)_2$ and $(C_2H_5)_2$. It is, however, difficult at the moment to determine from the spectrum alone whether the pyridine solvate is five- or six-coordinated.

It is interesting to point out that the behaviour of $Cu(X\text{-}sal.2,6\text{-}Y_2Ph)_2$ in pyridine is different

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[8] S. Yamada and H. Nishikawa, This Bulletin, **38**, 683 (1965).

[9] S. Yamada and E. Yoshida, *ibid.*, **40**, 1298, 1854 (1967); Proceedings Tenth International Conference on Coordination Chemistry (X. ICCC) (Tokyo, 1967), p. 275.

[10] M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, **40**, 27 (1957); R. L. Belford and T. S. Piper, *Mol. Phys.*, **5**, 251 (1962).

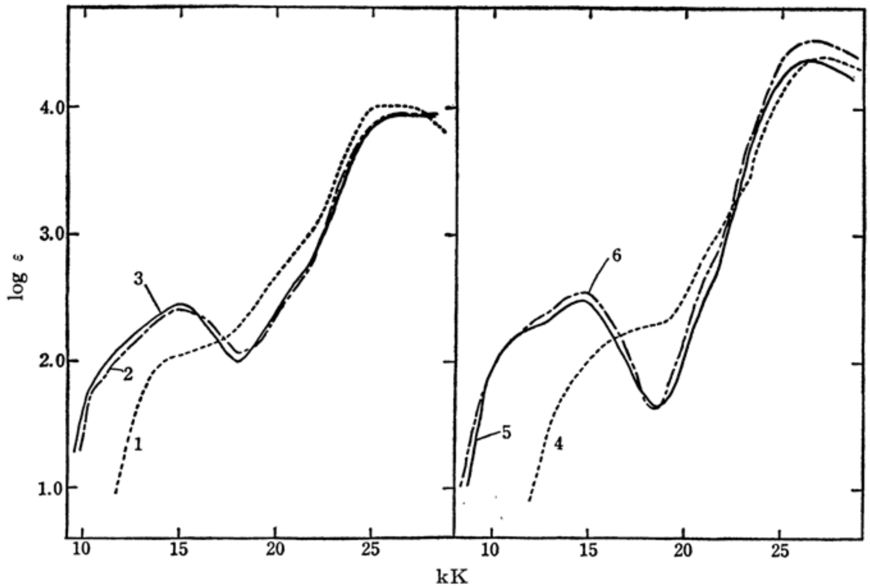

Fig. 5. Electronic absorption spectra of Cu(X-sal.2,6-Y_2Ph)$_2$ in solution.
1, X=5-Cl, Y=CH_3, in chloroform; 2, X=5-Cl, Y=CH_3, in pyridine; 3, X=5-Cl, Y=C_2H_5, in pyridine; 4, X=5-NO_2, Y=CH_3, in chloroform; 5, X=5-NO_2, Y=CH_3, in pyridine; 6, X=5-NO_2, Y=C_2H_5 in pyridine

from that of the corresponding nickel(II) complexes when X denotes H, 5-Cl, 5-Br and 5,6-benzo. This may also be considered to be an example showing that the coordination number larger than four in copper(II) complexes occurs at a slightly weaker ligand field than in the corresponding nickel(II) complexes.[2,11] This difference between the nickel(II) and the copper(II) complexes may be discussed in terms of the bonding nature of the metal ions and the steric condition arising from the two alkyl groups.[2]

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11) S. Yamada, H. Nishikawa, Y. Kuge and K. Yamanouchi, *Sci. Reports Coll.Gen. Educ., Osaka Univ.,* **16**, 11 (1967).