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Nickel(II) and Copper(II) Complexes of β-Ketoamines Derived from β-Diketones and Aromatic Amines[1]

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Nickel(II) and copper(II) complexes of β-ketoamines derived from acetylacetone or benzoylacetone and aromatic amines have been newly synthesized and characterized. The aromatic amines included aniline, *o*-, *m*- and *p*-toluidine, *o*, *o*′-dimethylaniline, *o*, *o*′-diethylaniline, *o*-, *m*- and *p*-chloroaniline, and α- and β-naphthylamine. The configurations of these complexes in pyridine have been examined and compared with those in non-donor solvents. All these complexes are considered to be square-planar in non-donor solvents and in the solid state. The nickel(II) complexes of the *o*, *o*′-disubstituted derivatives do not combine with pyridine molecules, whereas the corresponding copper(II) complexes readily combine with the pyridine molecule. The difference between nickel(II) and copper(II) ions is discussed in terms of the bonding nature of the metal ions. The β-ketoamines and salicylideneimines are also compared.

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[1] Presented in part at the 8th International Conference on Co-ordination Chemistry (8th ICCC), Vienna, September, 1964; The Proceedings, 8th ICCC (1964), p. 373.

Studies of nickel(II) and copper(II) complexes of Schiff bases derived from salicylaldehyde have so far been carried out by a number of investigators, yielding many conclusions which are of significance to the co-ordination chemistry of these metal ions. At that stage, it was thought to be interesting to compare the complexes of salicylideneimines with the corresponding complexes of β-ketoamines, such as acetylacetone- and benzoylacetoneamines (Fig. 1).[2,3] However, no systematic study has been carried out on the synthesis and characterization of these complexes.

In the present work, a series of new copper(II) and nickel(II) complexes have been synthesized with the β-ketoamines derived from aromatic amines and β-diketones. Then their configurations in pyridine have been examined and compared with the configurations in non-donor solvents, in order to establish the ability of the metal ions to combine with additional ligands at the residual co-ordination sites of the quadri-co-ordinate complexes. Copper(II) and nickel(II) have also been compared as the central metal ion, as the β-ketoamines and the salicylideneimines have been compared as the ligand. This kind of examination is particularly significant for the *N*-*o*, *o*′-disubstituted phenyl-derivatives, since these complexes might behave differently from the *N*-monosubstituted phenyl derivatives due to the steric condition, and so a comparison would yield important information about the co-ordination chemistry of these metal ions. Several new complexes of nickel(II) and copper(II) with salicylideneimines have also been synthesized in the present work.

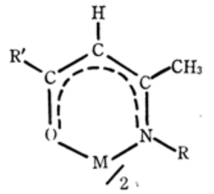

Fig. 1. Metal(II) complexes of β-ketoamines with $R' = CH_3$ or C_6H_5.

Experimental

Materials.—Bis(*N*-substituted acetylacetoneaminato)-nickel(II) complexes were prepared by the general method given below. Into a warm solution of nickel(II) acetate (0.01 mol.) and the ligand (0.012—0.013 mol.) in ethanol (15—20 ml.), a solution of potassium ethanolate was stirred drop by drop; this solution had been prepared, in advance, by adding potassium metal (0.022—0.024 g. atom) into ethanol (15—20 ml.). The reaction was then continued at about 70°C for two to six hours, depending upon the ligands used.

TABLE I. ELEMENTAL ANALYSES OF BIS(*N*-SUBSTITUTED ACETYLACETONEAMINATO)NICKEL(II) AND COPPER(II), $(CH_3\cdot CO\cdot CH\cdot \underset{CH_3}{\underset{|}{C}}\cdot NR)_2M$

R	Calcd. %			Found, %		
M=Ni(II)	C	H	N	C	H	N
C_6H_5	64.93	5.90	6.88	64.36	5.81	6.84
o-$CH_3C_6H_4$	66.27	6.44	6.44	66.70	6.66	6.57
p-$CH_3C_6H_4$				66.63	6.47	6.54
o, *o*′-$(CH_3)_2C_6H_3$**	67.41	6.96	6.05	67.70	6.83	6.22
o, *o*′-$(C_2H_5)_2C_6H_3$	69.40	7.71	5.40	68.01	7.72	6.09
o-ClC_6H_4	54.50	4.62	5.89	55.57	4.72	5.93
m-ClC_6H_4*				55.79	4.77	5.90
p-ClC_6H_4				55.43	4.77	5.90
α-Naphthyl	71.03	5.56	5.52	71.06	5.71	5.55
β-Naphthyl				70.84	5.72	5.61
M=Cu(II)						
p-$CH_3C_6H_4$	65.52	6.37	6.37	64.95	6.45	6.20
o, *o*′-$(CH_3)_2C_6H_3$	66.71	6.89	5.99	66.10	7.00	6.21
o, *o*′-$(C_2H_5)_2C_6H_3$	69.03	7.29	5.31	68.31	7.74	5.39
o-ClC_6H_4	54.94	4.58	5.83	54.71	4.73	5.45
m-ClC_6H_4*				54.97	4.68	5.81
p-ClC_6H_4				55.02	4.72	5.75
α-Naphthyl	70.38	5.57	5.34	70.36	5.51	5.47

* Recrystallized from ethyl ether.

** Recrystallizable from ethanol, according to Ref. 4b. However, the complex is scarcely soluble in ethanol, and the recrystallization has been carried out from benzene in the present work.

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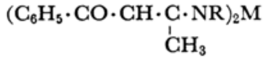
[2] As a matter of convenience, these ligands will be referred to as β-ketoamines in the present paper.

[3] Abbreviated in this paper as $M(Sal. R)_2$, $M(Aca. R)_2$, and $M(Bza. R)_2$ respectively.

TABLE II. ELEMENTAL ANALYSES OF BIS(*N*-SUBSTITUTED BENZOYLACETONEAMINATO)NICKEL(II) AND COPPER(II),



$(C_6H_5 \cdot CO \cdot CH \cdot \underset{CH_3}{\underset{|}{C}} \cdot NR)_2M$

R	Calcd. %			Found, %		
M=Ni(II)	C	H	N	C	H	N
C_6H_5	72.37	5.27	5.27	71.66	5.23	5.17
o-$CH_3C_6H_4$	73.03	5.73	5.01	72.15	5.82	4.85
p-$CH_3C_6H_4$				72.98	5.86	4.95
o, o'-$(CH_3)_2C_6H_3$*	73.63	6.14	4.77	73.82	6.37	4.77
o, o'-$(C_2H_5)_2C_6H_3$	74.68	6.84	4.36	74.90	6.97	4.47
o-ClC_6H_4	64.03	4.34	4.67	64.22	4.42	4.58
m-ClC_6H_4				63.67	4.26	4.62
p-ClC_6H_4				64.24	4.52	4.73
M=Cu(II)						
o-$CH_3C_6H_4$	72.40	5.68	4.97	72.43	5.83	4.99
m-$CH_3C_6H_4$				72.30	5.70	4.92
p-$CH_3C_6H_4$				72.12	5.86	4.90
o, o'-$(CH_3)_2C_6H_3$	73.03	6.09	4.73	71.54	6.21	4.56
o, o'-$(C_2H_5)_2C_6H_3$	74.13	6.80	4.32	73.67	6.91	4.43
o-ClC_6H_4	63.52	4.30	4.63	63.00	4.41	4.52
m-ClC_6H_4				62.95	4.28	4.47
p-ClC_6H_4				63.09	4.31	4.50

* Yellow-brown (light green, according to Ref. 4b)

TABLE III. ELEMENTAL ANALYSES OF BIS(*N*-SUBSTITUTED SALICYLIDENEIMINATO)NICKEL(II) AND COPPFR(II), $(Sal.NR)_2M$

R	Calcd. %			Found, %		
M=Ni(II)	C	H	N	C	H	N
o, o'-$(CH_3)_2C_6H_3$	67.41	6.96	6.05	67.70	6.83	6.22
o, o'-$(C_2H_5)_2C_6H_3$	72.52	6.39	4.97	71.59	6.25	4.90
α-Naphthyl	71.03	5.56	5.52	71.06	5.71	5.55
β-Naphthyl				70.84	5.72	5.61
p-ClC_6H_4	55.50	4.66	5.88	55.43	4.77	5.90
o, p, o'-$Cl_3C_6H_2$	47.46	2.15	4.26	47.81	2.16	4.15
o, p, o'-$Br_3C_6H_2$	33.77	1.53	3.03	33.81	1.60	3.15
M=Cu(II)						
o, m-$(CH_3)_2C_6H_3$	70.36	5.51	5.47	70.30	5.44	5.71
o, p-$(CH_3)_2C_6H_3$				70.39	5.54	5.52
o, o'-$(CH_3)_2C_6H_3$				70.30	5.50	5.40
o, o'-$(C_2H_5)_2C_6H_3$	71.91	6.34	4.93	71.84	6.35	4.91
o, p, o'-$Cl_3C_6H_2$	47.12	2.13	4.23	47.34	2.10	4.23
o, p, o'-$Br_3C_6H_2$	33.60	1.52	3.01	33.78	1.66	3.13

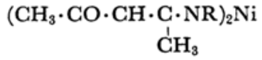
When the solution was cooled, crude crystals of the compound separated out. Pure crystals of the compound were obtained by the recrystallization of the crude product from suitable solvents. Prior to the above procedure, the ligand had generally been prepared by refluxing a mixed solution of the β-diketone and the amine on a water-bath for many hours. The elemental analyses of these compounds are given in Table I. These complexes are green.

Bis(*N*-substituted acetylacetoneaminato)copper(II) complexes were prepared in the same way as were the corresponding nickel(II) complexes, except that the reaction period with the copper(II) complexes was generally longer. The crystals which separated out were quickly filtered, washed, generally with ethanol, and dried in a vacuum desiccator. The elemental analyses of these compounds are shown in Table I. Most of these complexes are dark-brown or dark-green.

Bis(*N*-substituted phenyl-benzoylacetoneaminato)-nickel(II) complexes were prepared in a way similar to that used for the corresponding bis(acetylacetoneaminato)nickel(II) complexes. The elemental analyses are shown in Table II. These complexes are green or brownish green.

Bis(*N*-substituted phenyl-benzoylacetoneaminato)-copper(II) complexes were prepared in a way similar to that used for the corresponding bis(benzoylacetoneaminato)nickel(II) complexes. The elemental analyses are shown in Table II. These complexes are dark-brown.

TABLE IV. ABSORPTION MAXIMA OF BIS(*N*-SUBSTITUTED ACETYLACETONEAMINATO)NICKEL(II),

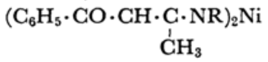


$$(CH_3\cdot CO\cdot CH\cdot \underset{CH_3}{\underset{|}{C}}\cdot NR)_2Ni$$

R	Solvent	ν 10^3 cm^{-1}	log ε	ν 10^3 cm^{-1}	log ε
o-$CH_3C_6H_4$	$CHCl_3$	16.7	1.54	sh*	
	py**	10.0	0.90	17.0	1.25
p-$CH_3C_6H_4$	$CHCl_3$	17.0	1.63	sh	
	py	10.4	1.19	17.3	1.17
o, o′-$(CH_3)_2C_6H_3$	$CHCl_3$	16.6	1.70	20.5	1.96
	py	16.5	1.68	20.9	1.96
o, o′-$(C_2H_5)_2C_6H_3$	$CHCl_3$	16.6	1.57	20.7	1.89
	py	16.6	1.62	20.8	1.89
α-Naphthyl	$CHCl_3$	16.4	1.74	20.5	2.05
	py	9.9	1.22	16.8	1.27
β-Naphthyl	$CHCl_3$	16.4	1.71	sh	
	py	10.4	1.29	17.6	1.59
o-ClC_6H_4	$CHCl_3$	16.6	1.69	20.7	1.90
	py	10.4	1.18	17.2	1.20
m-ClC_6H_4	$CHCl_3$	16.6	1.68	20.8	1.91
	py	10.5	1.25	17.4	1.18
p-ClC_6H_4	$CHCl_3$	16.4	1.70	20.7	1.94
	py	10.1	1.26	17.0	1.17

* sh: shoulder ** pyridine=py

TABLE V. ABSORPTION MAXIMA OF BIS(*N*-SUBSTITUTED BENZOYLACETONEAMINATO)NICKEL(II),



$$(C_6H_5\cdot CO\cdot CH\cdot \underset{CH_3}{\underset{|}{C}}\cdot NR)_2Ni$$

R	Solvent	ν 10^3 cm^{-1}	log ε	ν 10^3 cm^{-1}	log ε
o-$CH_3C_6H_4$	$CHCl_3$	16.2	1.81	sh*	
	py**	10.6	1.20	17.4	1.74
p-$CH_3C_6H_4$	$CHCl_3$	16.1	1.76	sh	
	py	10.3	1.11	17.6	1.39
o, o′-$(CH_3)_2C_6H_3$	$CHCl_3$	16.6	1.78	sh	
	py	16.4	1.70	sh	
o, o′-$(C_2H_5)_2C_6H_3$	$CHCl_3$	16.3	1.75	sh	
	py	16.1	1.70	sh	
o-ClC_6H_4	$CHCl_3$	16.0	1.80	sh	
	py	10.3	1.19	17.6	1.46
m-ClC_6H_4	$CHCl_3$	16.0	1.78	sh	
	py	16.5	1.24	17.6	1.68
p-ClC_6H_4	$CHCl_3$	16.5	1.82	sh	
	py	10.8	1.16	17.7	1.18

* sh: shoulder ** pyridine=py

The solvents used for the recrystallization of all the above complexes were mostly benzene and ethanol, although acetone and chloroform were occasionally employed.

The following complexes were reported previously[4]: Ni(Aca. *o, o′*-$(CH_3)_2C_6H_3)_2$, Ni(Bza. $C_6H_5)_2$, Cu(Aca. $C_6H_5)_2$, Cu(Aca. *o, o′*-$(CH_3)_2C_6H_3)_2$ and Cu(Bza. $C_6H_5)_2$. The methods of the preparation in the present work are different from that employed previously, except for that for the first complex. A paper has recently been presented describing the *N*-alkyl substituted β-ketoamine complexes of nickel(II).[5]

Bis(*N*-substituted phenyl-salicylideneiminato)complexes were prepared by reactions between the bis(salicylaldehyde)metal complex and one of the aromatic amines in ethanol or methanol. These complexes are dark-brown or dark-green.

For the preparation of *o, p, o′*-trichlorophenyl-substituted complexes of this series, a solution of the Schiff base, which had been prepared in advance, was added to copper acetate or nickel acetate in ethanol,

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[4] a) A. S. Kudryavtsev and I. A. Savich, *Vestn. Moskow Univ. Ser. II. Khim.*, **18** (**4**), 61 (1963). b) T. M. Hseu, D. F. Martin and T. Moeller, *Inorg. Chem.*, **2**, 587 (1963).

[5] G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965).

and then the solid sodium hydrogen carbonate was added. The reaction was continued at 60—70°C for several hours. The elemental analyses are shown in Table III. These complexes are all brown or green.

The other complexes discussed in the present paper were prepared according to the methods previously reported. Elemental analyses for carbon, hydrogen and nitrogen agreed with the formulae given previously.

Measurements.—The electronic absorption spectra of the complexes in solution were determined with a Shimadzu QR 50 spectrophotometer and a Beckman DU spectrophotometer. Pyridine for a solvent was purified by distillation after it had been boiled for some hours over barium oxide.

The diamagnetism of the nickel(II) complexes in the solid state was detected by Gouy's method.

Results and Discussion

The Nickel(II) Complexes of β-Ketoamines and Salicylideneimines Derived from Aromatic Amines.—Numerous new nickel(II) complexes of the ketoamines have been prepared in the present work; they are shown in Tables I, II and III, together with several new complexes of salicylideneimines. In general, the preparation of the metal complexes of the β-ketoamines was found to be more difficult in many ways than the preparation of the corresponding complexes of the salicylideneimines.

The fact that all these nickel(II) complexes of the β-ketoamines are diamagnetic in the solid state indicates the planar configuration of these complexes. It is now well known that the electronic spectrum of a nickel(II) complex varies remarkably according as the nickel(II) complex is square-planar, tetrahedral or octahedral.[6,7] Consequently, the spectrum may be regarded as symptomatic of the configuration of the nickel(II) complex. Thus, the present measurements clearly indicate that the electronic spectra of the complexes of $Ni(Aca.aryl)_2$ and $Ni(Bza.aryl)_2$ types in chloroform or benzene are characteristic of the square-planar nickel(II) complex (Figs. 2 and 3).[8] There is controversy about the assignment of the absorption bands of square-planar nickel(II) complexes,[9] but a tentative assignment may be ^1A_g—$^1B_{1g}$ and ^1A_g—$^1B_{3g}$ for the absorption bands at about 16.5 and 20.5×10^3 cm^{-1} respectively. These complexes show no absorption 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, at least near room temperature. The same conclusion was obtained with a solution of a very high concentration. Comparison clearly shows that the tendency of the square-planar complexes to form associated polymers in solution is much lower with the β-ketoamine complexes than with the corresponding salicylideneimine complexes, since the previous studies[6] have shown that bis(*N*-monosubstituted phenylsalicylideneiminato)-nickel(II) complexes in non-donor solvents consist of the square-planar monomer, the associated polymer with the sexa-co-ordinated nickel(II), and the tetrahedral monomer, the former two being in equilibrium with each other near room temperature. This difference between the β-ketoamine and the salicylideneimine complexes may be due to the stronger ligand field produced by the β-ketoamines, since the stronger ligand field will increase the energy difference between the $d_{x^2-y^2}$ orbital and the next highest orbital of the nickel(II) ion, making the highest $d_{x^2-y^2}$ orbital less readily occupied in the formation of the sexa-co-ordinated nickel(II).[10]

In order to examine the effect of the two substituents at the *o*- and *o'*-carbon atoms on the residual co-ordination sites, the electronic absorption spectra of the compounds were examined in pyridine, and compared with the results for the corresponding complexes with monosubstituted radicals. With the exception of the *o*, *o'*-disubstituted complexes, all the nickel(II) complexes examined were found to take up two pyridine molecules, as may be seen from their electronic spectra (Figs. 2 and 3, and Tables IV and V). The absorption bands at about 10 and 16.5×10^3 cm^{-1} are tentatively identified as $^3A_{2g}\rightarrow{}^3T_{2g}$ and $^3A_{2g}\rightarrow{}^3T_{2g}$ (F) for the octahedral nickel(II) complexes. The spectra obtained, which are remarkably different from the spectra of the tetrahedral and the square-planar complexes of nickel(II), have the main features characteristic of the sexa-co-ordinated nickel(II) complexes.[6,7,11] Since Beer's law is generally obeyed, an equilibrium between the octahedral complex and another species may be excluded. It should be noted that even the *o*-monosubstituted complexes form sexa-co-ordinated complexes by taking up two pyridine molecules for the complexes of the $Ni(Sal.R)_2$, $Ni(Aca.R)_2$ and $Ni(Bza.R)_2$ types. This is also found to be the case with the complexes having α-naphthyl for R.

On the contrary, the spectra of the *o*, *o'*-disubstituted nickel(II) complexes of salicylideneimines, acetylacetoneamines and benzoylacetoneamines in pyridine are very similar to the spectra of the same compounds in chloroform (Figs. 2 and 3, and Tables IV and V). It is clear that

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[6] L. Sacconi, "Essays in Co-ordination Chemistry" (Eds. W. Schneider, G. Anderegg and R. Gut), Birkhauser Verlag, Basel (1964), p. 148; R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).

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

[8] In general, the electronic spectra of these complexes in benzene or ethanol are essentially the same as those in chloroform.

[9] G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958); J. Ferguson, ibid., **34**, 611 (1961). Another assignment is given by A. D. Liehr and C. J. Ballhausen, *J. Am. Chem. Soc.*, **81**, 538 (1959).

[10] A. B. P. Lever, The Proceedings, 8th ICCC (1964), p. 123.

[11] A pyridine adduct of bis(*N*-phenyl-salicylideneiminato)-nickel(II) was reported previously. L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 1750 (1963).

the square-planar configuration of these complexes is held in pyridine as well as in chloroform. Neither the sexa-co-ordinated form combining the two pyridine molecules nor the tetrahedral form is present, since there is no absorption in the frequency region lower than 700 mμ, except for a very feeble absorption band which may be ascribed to the singlet-triplet(spin-forbidden) transition of

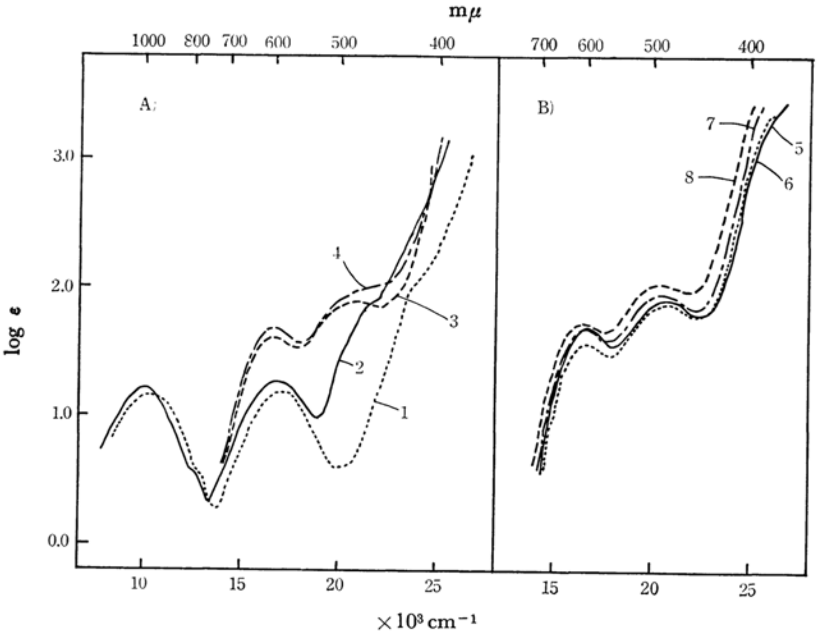

Fig. 2. Electronic absorption spectra of Ni(Aca.R)$_2$. (A) In pyridine : 1, R$=o$-ClC$_6$H$_4$ (---------); 2, R$=\alpha$-naphthyl (——); 3, R$=o,o'$-(C$_2$H$_5$)$_2$C$_6$H$_3$ (— — —); 4, R$=o,o'$-(CH$_3$)$_2$C$_6$H$_3$(—-—-); and (B) in chloroform: 5, R$=o$-ClC$_6$H$_4$ (——); 6, R$=o,o'$-(C$_2$H$_5$)$_2$C$_6$H$_3$ (---------); 7, R$=o,o'$-(CH$_3$)$_2$C$_6$H$_3$ (—-—-); 8, R$=\alpha$-naphthyl (— — —).

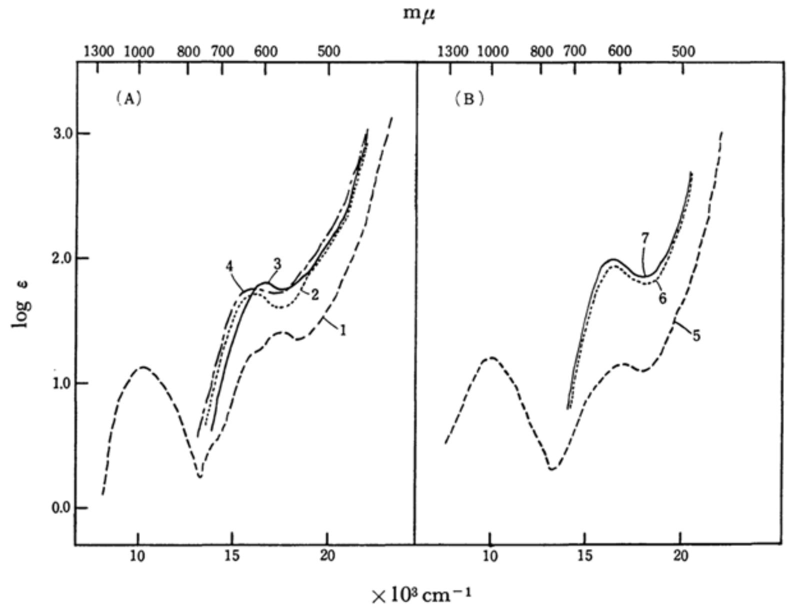

Fig. 3. Electronic absorption spectra of (A) Ni(Bza.R)$_2$: 1, R$=p$-CH$_3$C$_6$H$_4$ in pyridine (— — —); 2, R$=o,o'$-(C$_2$H$_5$)$_2$C$_6$H$_3$ in pyridine (---------); 3, R$=o,o'$-(CH$_3$)$_2$C$_6$H$_3$ in chloroform (——); 4, R$=p$-CH$_3$C$_6$H$_4$ in chloroform (—-—-) and (B) Ni(Sal.R)$_2$: 5, R$=p$-CH$_3$C$_6$H$_4$ in pyridine (— — —); 6, R$=o,o'$-(C$_2$H$_5$)$_2$C$_6$H$_3$ in pyridine (---------); 7, R$=o,o'$-(C$_2$H$_5$)$_2$C$_6$H$_3$ in chloroform (——).

the square-planar complex. The fact that no association of the square-planar complexes takes place may be interpreted on the basis of the steric hindrance due to the two methyl or ethyl groups at the *o*- and *o*′-positions.

The Copper(II) Complexes of β-Ketoamines and Salicylideneimines Derived from Aromatic Amines.—Many new copper(II) complexes

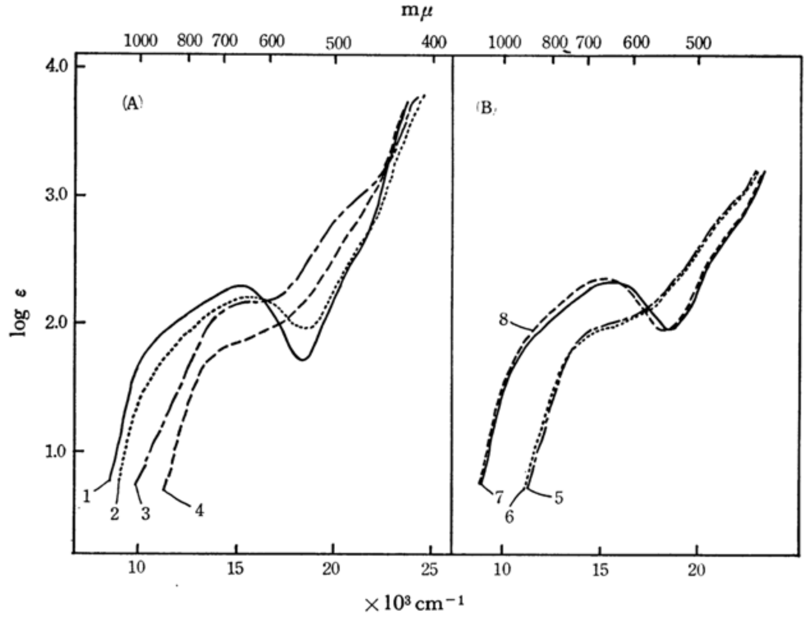

Fig. 4. Electronic absorption spectra of (A) $Cu(Sal.R)_2$: 1, R=o,p,o'-$Cl_3C_6H_2$ in pyridine(——); 2, R=o-$CH_3C_6H_4$ in pyridine (---------); 3, R=o-$CH_3C_6H_4$ in chloroform (—-—-); 4, R=o,p,o'-$Cl_3C_6H_2$ in chloroform (— — —) and (B) $Cu(Sal.R)_2$: 5, R=o,o'-$(C_2H_5)_2C_6H_3$ in chloroform (——); 6, R=o,o'-$(CH_3)_2C_6H_3$ in chloroform (---------); 7, R=o,o'-$(CH_3)_2C_6H_3$ in pyridine (——); 8, R=o,o'-$(C_2H_5)_2C_6H_3$ in pyridine(— — —).

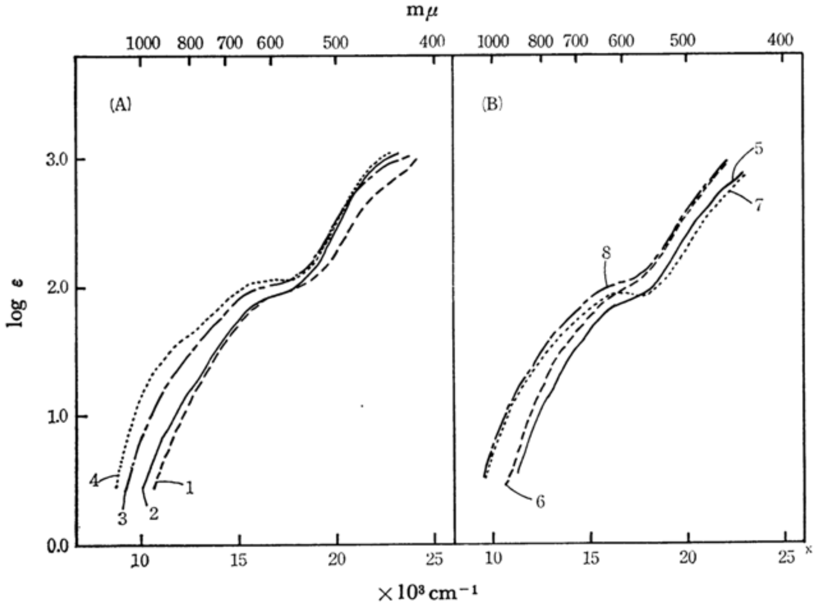

Fig. 5. Electronic absorption spectra of (A) $Cu(Aca.R)_2$: 1, R=o,o'-$(C_2H_5)_2C_6H_3$ in chloroform (---------); 2, R=o,o'-$(CH_3)_2C_6H_3$ in chloroform (——); 3, R=o,o'-$(C_2H_5)_2C_6H_3$ in pyridine (—-—-); 4, R=o,o'-$(CH_3)_2C_6H_3$ in pyridine (---------); and (B) $Cu(Bza.R)_2$: 5, R=o,o'-$(CH_3)_2C_6H_3$ in chloroform (——); 6, R=o,o'-$(C_2H_5)_2C_6H_3$ in chloroform (— — —); 7, R=o,o'-$(CH_3)_2C_6H_3$ in pyridine (---------); 8, R=o,o'-$(C_2H_5)_2C_6H_3$ in pyridine (—-—-).

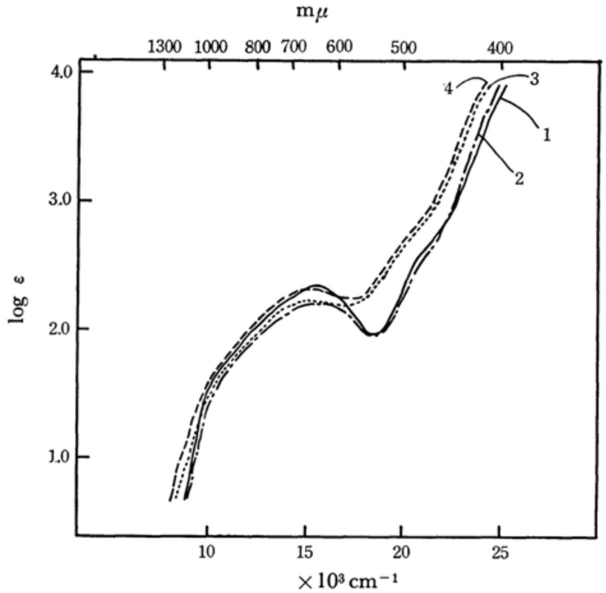

Fig. 6. Electronic absorption spectra of $Cu(Sal.R)_2$ in pyridine : 1, R=o,o'-$(CH_3)_2C_6H_3$ (——); 2, R=o-$CH_3C_6H_4$ (—-—-); 3, R=p-$CH_3C_6H_4$ (---------); 4, R=m-$CH_3C_6H_4$ (—·—·—).

of the β-ketoamines and salicylideneimines, which are shown in Tables I, II and III, have been prepared in the present work. The planar configuration is most likely for the copper(II) complexes, since the tendency of the copper(II) complex to take the square-planar configuration is known to be very great. The square-planar configuration can not be rejected, even for the o, o'-disubstituted complexes of copper(II), on the steric ground alone, since the corresponding complexes of nickel(II) have been found to be square-planar. It is reasonable to presume that the o, o'-disubstituted and the monosubstituted complexes of copper(II) take a square-planar configuration. This presumption seems to be consistent with the present observation that the o, o'-disubstituted and the monosubstituted complexes of copper(II) show ligand field bands at a nearly identical frequency, and that the whole pattern of the spectra is also quite similar among these complexes (Fig. 4). It was previously shown that the ligand field band was shifted toward a considerably lower frequency when the cupric complex was distorted appreciably from the square-planar configuration.[6,7]

The change in the ligand field band of these copper(II) complexes on going from chloroform to pyridine, the change shown in Figs. 4 and 5, is similar to the change observed previously when the quadri-co-ordinated complex of copper(II) takes up one or two additional ligands to form a quinque- or sexa-co-ordinated complex.[12] It may be concluded, therefore, that all the cupric complexes examined in the present work are combined with one or two pyridine molecules in the pyridine solution. The change in the spectrum of the complex on going from chloroform to pyridine is more pronounced for the salicylideneimine complexes than for the corresponding β-ketoamine complexes.

Judging from the steric effect due to the two substituents, it is most likely that the o, o'-disubstituted complexes are able to take only one molecule of pyridine to form a quinque-co-ordinated configuration. It should be noted that the spectral behavior of the o, o'-disubstituted complexes of copper(II) in pyridine is quite similar to that of the corresponding monosubstituted complexes, and that the monosubstituted complexes of copper(II) in pyridine show spectra almost superposable on those of the corresponding disubstituted complexes (Figs. 5 and 6). The spectral change on going from chloroform to pyridine is also similar for these complexes. It is most likely that all these copper(II) complexes, therefore, take an identical configuration in pyridine. This seems to be in agreement with a previous finding concerning the ability of bis(acetylacetonato)copper(II) to combine with another ligand such as pyridine.[13]

Comparison of Nickel(II) with Copper(II). —It has been found in the present work that, in the binding of the additional pyridine molecule, the o, o'-disubstituted complexes of copper(II) are different from the corresponding complexes of nickel(II); the nickel(II) complexes combine

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

[13] D. P. Graddon, *J. Inorg. Nucl. Chem.*, **17**, 222 (1961); D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1963**, 5885.

with no additional pyridine molecule. This difference between copper(II) and nickel(II) may be interpreted in terms of the bonding nature of the metal ions and in terms of the steric condition of the ligands. In the complexes of copper(II) with a d^9 configuration, the copper-ligand bond distance along the z-direction is generally found to be appreciably longer, due to the Jahn-Teller effect, than the corresponding bond distance in the xy-plane, that is, the complex-plane. Moreover, quinque-co-ordinated complexes are not rare for the copper(II) ion. On the other hand, the six bonds between the nickel(II) ion and ligands are essentially equivalent in the sexa-co-ordinated complexes of nickel(II) with a d^8 configuration. It is, therefore, reasonable to expect that the two substituents at the *o*- and *o*′-positions may prevent the pyridine molecule from combining with the nickel(II) ion, whereas the copper(II) ion in the corresponding complex may combine with the pyridine molecule at a little farther distance in spite of the possible steric hindrance.

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