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Transition Metal Chelates of Bis(salicylidene-1,2-diaminoethylene) Derivatives

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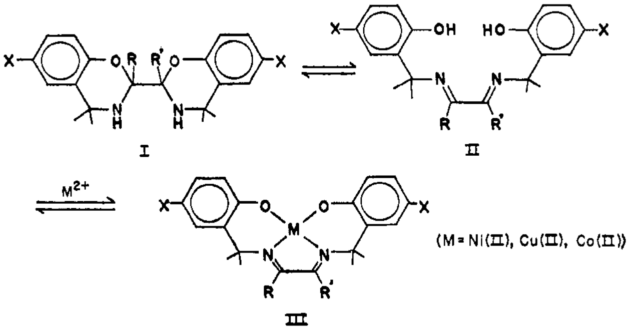
It was found previously that 2,2′-dialkyl-2,2′-bibenz-1,3-oxazine could isomerize by ring opening to a Schiff base, 1,6-bis-(2-hydroxyphenyl)-2,5-diaza-3,4-dialkyl-2,4-hexadiene, in some solution. Since the Schiff base was considered to be a quadridentate chelate ligand, the reactions of the oxazines with Ni(II), Cu(II), and Co(II) ions have been investigated in the hope of yielding metal chelates with the isomeric Schiff bases. The products were however found to be different from the expected one in the ligand structures. In the case of nickel, two kinds of chelates were obtained. Those formed in the absence of air were determined to be 1,6-bis(2-hydroxyphenyl)-2,5-diaza-3,4-dialkyl-1,4-hexadienatonickel(II) in which a proton migration from the original ligand had occurred and the others obtained in the presence of air were 1,6-bis(2-hydroxyphenyl)-2,5-dialkyl-1,3,5-hexatrienatonickel(II) in which dehydrogenation had proceeded on the original ligand. The Cu(II) and the Co(II) chelates were determined to have the same ligand structures as the latter of the Ni(II) chelates. The formation and the structure determination of these novel chelates are described and the formation mechanisms are discussed.

Introduction

In the previous paper,[1] we reported the synthesis of a series of new heterocycles, 2,2′-bibenz-1,3-oxazines I, and found in the course of their proton magnetic resonance studies that these oxazines existed as an equilibrium mixture with the tautomeric Schiff bases II in such a polar solvent as pyridine.

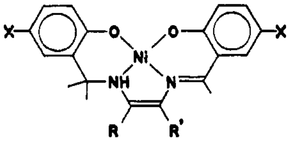
SCHEME I

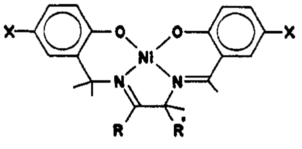


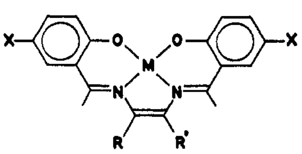
	R	R′	X
Ia	CH_3	CH_3	H
Ib	$CH_2CH_2CH_2CH_2$		H
Ic	$CH_2CH_2CH_2CH_2$		Cl
Id	CH_3	CH_3	$C(CH_3)_3$
Ie	$CH_2CH_2CH_2CH_2$		$C(CH_3)_3$

It was expected from the viewpoint of coordination chemistry that the Schiff base species II would form metal chelates III because they have a good shape to behave as quadridentate ligands. The reactions of I (Ia–Ie) with Ni(II), Cu(II), Co(II), and Co(III) ions have been investigated under various conditions and metal chelates were successfully isolated as reddish crystals. However, it was found that the reactions involving proton migration or dehydrogenation had proceeded on the ligand molecules; as a result, these metal chelates were different from III in the structure expected.

With nickel, two types (Ni-A and Ni-B) of chelates were obtained, where the structure of Ni-A was determined to be V and that of Ni-B was found to be VI, respectively. In the case of copper and cobalt, the chelate structures were also given as VI for both as well as for Ni-B. The metal chelates obtained in this investigation are listed in Tables I and II with data of the elementary analysis.


IV


V


VI, M = Ni(II), Cu(II), Co(II)

This report deals with the synthesis of these metal chelates and the determination of the structures; the mechanisms of the chelate formation will be discussed.

Experimental Section

General Procedure for the Ni-A Chelate Synthesis (No. 1–5).[2]—Under nitrogen, the oxazine (Ia–Ie) was suspended in a small amount of methanol and an equimolar nickel(II) acetate in a minimum amount of warm methanol was added. The mixture was heated on a water bath, where the oxazine was gradually dissolved while reddish orange crystals began to form in few minutes. After a 3-hr reflux, the crystals were filtered (in the case of 1, a small amount of ether was added to induce crystallization) and washed with methanol under nitrogen. The yield was between 50 and 80% and the product may be recrystallized from pyridine in a nitrogen stream. The dried samples were stable against oxidation in an air atmosphere.

General Procedure for the Ni-B Chelate Synthesis (No. 7–10).—In an air atmosphere, 1 mol of the oxazine (Ia–Ie) was dissolved in a minimum amount of pyridine at room temperature, 2 mol of nickel(II) acetate in pyridine was added, and the mixture was heated on a water bath for 1 hr and was allowed to stand overnight at room temperature. The resulting deep red crystals were filtered and recrystallized from pyridine. The yield was around 70%. When an equimolar nickel(II) acetate was allowed to react, the yield was depressed to around 50%.

Each one of the same chelates listed above was also obtained in quantitative yield from the corresponding Ni-A by the recrystallization from pyridine in an air atmosphere.

General Procedure for the Cu(II) Chelated Synthesis (No. 12, 14, 16, 18, and 20).—To a suspension of 1 mol of the oxazine (Ia–Ie) in a small amount of methanol was added 2 mol of copper(II) acetate in warm methanol and the mixture was heated on a water bath. As the oxazine was dissolved, reddish brown crystals began to deposit. Heating was interrupted at this stage and the mixture was allowed to cool to room temperature.

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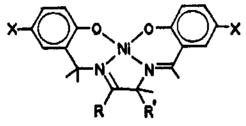
(1) H. Kanatomi and I. Murase, *Bull. Chem. Soc. Jap.*, **43**, 226 (1970).

(2) The numbers refer to Tables I and II.

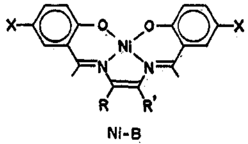
TABLE I

STRUCTURES AND ELEMENTARY ANALYSES OF Ni-A [1,6-BIS(2-HYDROXYPHENYL)-2,5-DIAZA-3,4-DIALKYL-1,4-HEXADIENATONICKEL(II)] AND Ni-B [1,6-BIS(2-HYDROXYPHENYL)-2,5-DIAZA-3,4-DIALKYL-1,3,5-HEXATRIENATONICKEL(II)]



Ni-A

No.	R	R′	X	Formula	% calcd			% found		
					C	H	N	C	H	N
1	CH_3	CH_3	H	$C_{18}H_{18}N_2O_2Ni \cdot 0.5H_2O$	59.71	5.29	7.73	59.95	5.31	7.66
2	$CH_2CH_2CH_2CH_2$		H	$C_{20}H_{20}N_2O_2Ni$	63.36	5.31	7.39	63.36	5.28	7.46
3	$CH_2CH_2CH_2CH_2$		Cl	$C_{20}H_{18}N_2O_2Cl_2Ni$	53.62	4.02	6.25	53.58	4.04	6.19
4	CH_3	CH_3	$C(CH_3)_3$	$C_{26}H_{34}N_2O_2Ni$	64.61	7.51	5.79	64.99	7.46	5.72
5	$CH_2CH_2CH_2CH_2$		$C(CH_3)_3$	$C_{28}H_{36}N_2O_2Ni \cdot 0.5H_2O$	67.21	7.45	5.59	66.80	7.22	5.58
6	CH_3	CH_3	Cl	$C_{18}H_{16}N_2O_2Cl_2Ni$	51.23	3.82	6.63	51.32	3.89	6.63

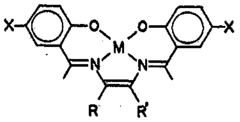


Ni-B

No.	R	R′	X	Formula	% calcd			% found		
					C	H	N	C	H	N
7	CH_3	CH_3	H	$C_{18}H_{16}N_2O_2Ni$	61.58	4.59	7.87	61.02	4.72	7.77
8	$CH_2CH_2CH_2CH_2$		H	$C_{20}H_{18}N_2O_2Ni$	63.87	4.82	7.44	63.70	4.99	7.48
9	CH_3	CH_3	$C(CH_3)_3$	$C_{26}H_{32}N_2O_2Ni$	67.40	6.96	6.04	67.58	7.09	6.05
10	$CH_2CH_2CH_2CH_2$		$C(CH_3)_3$	$C_{28}H_{34}N_2O_2Ni$	68.73	7.00	5.72	68.83	6.85	5.74
11	CH_3	CH_3	Cl	$C_{18}H_{14}N_2O_2Cl_2Ni$	51.46	3.36	6.66	51.47	3.52	6.45

TABLE II

STRUCTURES AND ELEMENTARY ANALYSES OF 1,6-BIS(2-HYDROXYPHENYL)-2,5-DIAZA-3,4-DIALKYL-1,3,5-HEXATRIENATOCOPPER(II) AND 1,6-BIS(2-HYDROXYPHENYL)-2,5-DIAZA-3,4-DIALKYL-1,3,5-HEXATRIENATOCOBALT(II)



M = Cu(II), Co(II)

No.	R	R′	X	Formula	% calcd			% found		
					C	H	N	C	H	N
12	CH_3	CH_3	H	$C_{18}H_{16}N_2O_2Cu$	60.75	4.53	7.87	60.19	4.55	7.80
13	CH_3	CH_3	H	$C_{18}H_{16}N_2O_2Co$	61.54	4.59	7.97	60.92	4.58	7.92
14	$CH_2CH_2CH_2CH_2$		H	$C_{20}H_{18}N_2O_2Cu$	62.90	4.75	7.34	62.94	4.91	7.45
15	$CH_2CH_2CH_2CH_2$		H	$C_{20}H_{18}N_2O_2Co$	63.87	4.82	7.44	63.74	5.05	7.54
16	$CH_2CH_2CH_2CH_2$		Cl	$C_{20}H_{16}N_2O_2Cl_2Cu$	53.28	3.57	6.21	52.91	3.70	6.13
17	$CH_2CH_2CH_2CH_2$		Cl	$C_{20}H_{16}N_2O_2Cl_2Co$	53.83	3.61	6.27	53.67	3.62	6.29
18	CH_3	CH_3	$C(CH_3)_3$	$C_{26}H_{32}N_2O_2Cu$	66.71	6.89	5.98	66.54	6.91	6.01
19	CH_3	CH_3	$C(CH_3)_3$	$C_{26}H_{32}N_2O_2Co$	67.38	6.95	6.04	67.67	6.97	6.10
20	$CH_2CH_2CH_2CH_2$		$C(CH_3)_3$	$C_{28}H_{34}N_2O_2Cu$	68.05	6.94	5.66	68.04	6.96	5.79
21	$CH_2CH_2CH_2CH_2$		$C(CH_3)_3$	$C_{28}H_{34}N_2O_2Co$	68.70	7.00	5.72	69.16	7.09	5.76
22	CH_3	C_2H_5	H	$C_{19}H_{18}N_2O_2Cu$	61.69	4.90	7.57	61.44	4.82	7.52
23	CH_3	CH_3	Cl	$C_{18}H_{14}N_2O_2Cl_2Co$	51.46	3.36	6.66	51.30	3.40	6.51

The resulting crystals were filtered and washed with methanol; yield ~80%. The products may be recrystallized from a chloroform–methanol mixture; however, they were pure enough without further purification. Prolonged heating of the reaction mixture resulted in the formation of a copper mirror on a wall of the flask and slightly reduced the yield. When 1 mol of copper(II) acetate was allowed to react, the yield was depressed to around 40%.

General Procedure for the Co(II) Chelate Synthesis (No. 13, 15, 17, 19, and 21).—With cobalt(II) acetate and the oxazine, the procedure was the same as the Ni-A synthesis and the Co(II) chelates were obtained generally in 30% yield. The same Co(II) chelates were obtained in about 50% yield when 1 mol of tris(acetylacetonato)cobalt(III) was allowed to react in place of cobalt(II) acetate under similar conditions.

Cu(II) Chelate of 1,6-Bis(2-hydroxyphenyl)-3-methyl-4-ethyl-2,5-diaza-1,3,5-hexatriene (No. 22).—A mixture of bis(salicylaminato)copper(II) (0.65 g, 2 mmol) and 2,3-pentanedione (0.2 g, 2 mmol) in 15 ml of methanol was refluxed for 4 hr in a nitrogen stream. Insoluble salicylidenesalicylaminatocopper(II) and copper metal which resulted as by-products were filtered and the filtrate was concentrated to 5 ml under reduced pressure. The resulting red-brown product was recrystallized from methanol; yield 50 mg (6.7%).

Ni(II) Chelate of 1,6-Bis(2-hydroxy-5-chlorophenyl)-3,4-dimethyl-2,5-diaza-1,4-hexadiene (No. 6).—To a warm solution of nickel(II) acetate (0.48 g, 2 mmol) in 20 ml of methanol, 5-chlorosalicylamine (0.6 g, 4 mmol) and 2,3-butanedione (0.18 g, 2.2 mmol) were added in this order and the mixture was refluxed for 4 hr in a nitrogen stream. The resulting red crystals were filtered and washed with methanol under nitrogen; yield 250 mg (30%).

Ni(II) Chelate of 1,6-Bis(2-hydroxy-5-chlorophenyl)-3,4-dimethyl-2,5-diaza-1,3,5-hexatriene (No. 11).—To a solution of 5-chlorosalicylamine (0.32 g, 2 mmol) and nickel(II) acetate (0.24 g, 1 mmol) in 15 ml of pyridine was added 2,3-butanedione (0.08 g, 1 mmol) and the mixture was heated on a water bath for 5 hr. The resulting red crystals were filtered and washed with methanol; yield 50 mg (12%).

Co(II) Chelate of 1,6-Bis(2-hydroxy-5-chlorophenyl)-3,4-dimethyl-2,5-diaza-1,3,5-hexatriene (No. 23).—With cobalt(II) acetate, the procedure was the same as that of 6, and dark red crystals were isolated in 20% yield.

Acid Hydrolysis of the Metal Chelates.—A weighed sample of the metal chelates (*ca.* 130 mg) was added to 10 ml of 4 *M* hydrochloric acid and the mixture was allowed to stand overnight at room temperature. The resulting clear solution was extracted three times each with 15 ml of ether and the combined ether extracts were dried over sodium sulfate and concentrated to 5 ml. To this was added 5 ml of a 2,4-dinitrophenylhydrazine solution (1 g of 2,4-dinitrophenylhydrazine in a mixture of 20 ml of methanol and 0.5 ml of concentrated sulfuric acid) and the mixture was allowed to stand overnight at room temperature. The resulting hydrazone was collected by filtration, dried over calcium chloride under vacuum at 50°, and then weighed. The salicylaldehyde 2,4-dinitrophenylhydrazone was identified with an authentic sample by a mixture melting point (250–251°) and by an infrared spectrum. The quantities of the salicylaldehyde obtained from 1 mol of the sample were nearly 1 mol for **2** (Ni-A) and 2 mol for **8** (Ni-B) and for **14** (Cu).

All the metal chelates obtained in this investigation were dried under vacuum over phosphorus pentoxide at 50° and their decomposition points were over 300°. The elementary analysis was carried out at the Service Center of Elementary Analysis, Kyushu University. The electronic spectra were measured in chloroform with a Hitachi EPS-3T and the infrared spectra were taken in KBr disks and in chloroform with a Hitachi EPI S2, while proton magnetic resonance spectra were recorded on a 60-MHz JEOL C-60H nmr spectrometer with tetramethylsilane as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer, using a direct inlet at 260° and at an ionization energy of 70 eV. The magnetic moments were measured at room temperature by means of a recording magnetometer specially designed by Hirakawa.[3]

Results and Discussion

Structures of the Ni(II) Chelates.—In the reactions of the oxazines (Ia–Ie) with the Ni(II) ion, each one gave two kinds of chelates to which Ni-A and Ni-B were tentatively denoted and either formation depended upon the reaction conditions. The reaction conducted in the absence of air (oxygen) afforded Ni-A and the reaction in an air atmosphere yielded Ni-B. Ni-A was air sensitive in solution and was easily converted to Ni-B upon recrystallization from pyridine in an air atmosphere.

The elementary analysis of each Ni-A was in good agreement with the molecular formula derived from the corresponding structure III. A mass spectrum of **2** showed a peak at *m/e* 378 (^{58}Ni) which was assigned to a parent molecular ion and corresponded to the molecular weight calculated for $C_{20}H_{20}N_2O_2Ni$. It seemed, so far, to be consistent to adopt the structure III for Ni-A; however, significant evidence which was inconsistent with III was found in its chemical properties. Upon hydrolysis of Ni-A in an acidic medium, 1 mol of salicylaldehyde was isolated as 2,4-dinitrophenylhydrazone. Because III has no possibility to give such species by the hydrolysis, an isomeric structure consisting of a salicylidene moiety should be considered and two possible structures (IV and V) could be postulated.

Although the infrared absorption spectra for all Ni-A compounds showed superimposable patterns in the double-bond region exhibiting the bands around 1650, 1620, 1600, 1570, and 1530 cm^{-1} and indicating the structural identity, they cannot be used diagnostically for the structure assignment in this case. However, the imino structure (IV) should be excluded from the possibilities, because no absorption was observed around 3100–3500 cm^{-1} where an NH stretching vibration would appear. On the other hand, the assignment of pmr spectra for Ni-A was consistent for the all protons in case V had been assumed.

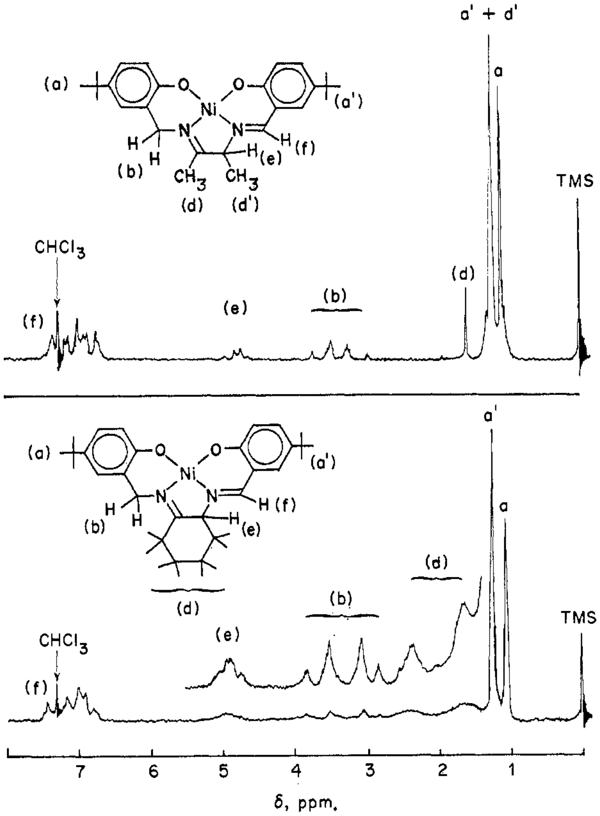


Figure 1.—The pmr spectra of Ni-A chelates in $CDCl_3$: **4**, upper; **5**, lower.

The pmr spectrum of **4** (Ni-A) is shown in Figure 1.[4] The sharp peaks at 1.13 and 1.26 ppm correspond to 21 protons and these are due to the *tert*-butyl protons (a and a′). The splitting of the resonance suggests unequal magnetic environments in these two groups and the asymmetric feature of the ligand can be realized. The resonance of the methyl protons (d) appears at 1.63 ppm and the other (d′) which will be expected to appear at higher field as a doublet by a coupling with the vicinal proton (e) must be eclipsed by one of the *tert*-butyl signals at 1.26 ppm. A quartet AB-type pattern centered at 3.53 ppm (J_{AB} = 15 Hz) corresponding to two protons is assigned to the methylene group (b), and a weak quartet of signals at 4.85 ppm (J = 6 Hz) is due to the proton (e) on the ethylenic carbon atom which couples with the vicinal methyl protons (d′). The azomethine proton (f) resonates at 7.46 ppm which is partially overlapped with the signals of the protons on the phenyl rings.

Although the spectrum of **5** was less precise than the above, it exhibits a similar pattern as seen in Figure 1. The protons (a and a′) of the two unequivalent *tert*-butyl groups appear as two separate singlets at 1.13 and 1.27 ppm partially overlapped with the cyclohexyl proton (d) resonances, the AB-type quartet centered at 3.36 ppm (J = 14 Hz) is due to the benzyl methylene (b), and the weak signals at 4.85 ppm can be assigned to a proton (e) on the cyclohexyl carbon adjacent to the azomethine nitrogen. The azomethine proton (f) resonance appears at 7.42 ppm partially overlapped with the signals of the phenyl ring protons, as well as in the case of **4**.

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[3] K. Hirakawa, Ka. Hirakawa, and S. Yoneyama, *Jap. J. Appl. Phys.*, **2**, 816 (1963).

[4] The pmr measurement was only possible for **4** and **5** in Ni-A because of the poor solubility of the others in the solvent.

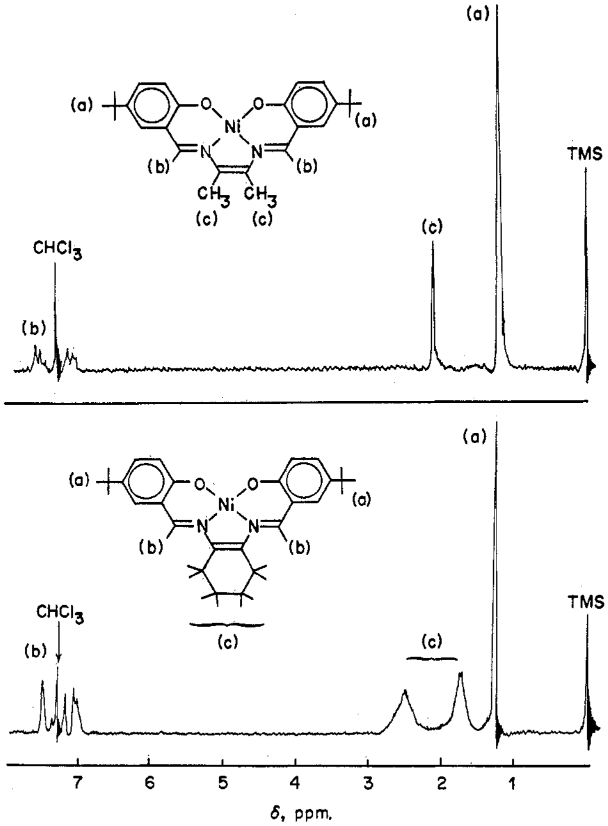

Figure 2.—The pmr spectra of Ni-B chelates in $CDCl_3$: **9**, upper; **10**, lower.

It was concluded from this evidence that the structure of Ni-A should be V, *i.e.*, 1,6-bis(2-hydroxyphenyl)-2,5-diaza-3,4-dialkyl-1,4-hexadienatonickel(II).

Ni-B chelates are very stable in contrast with those of Ni-A. They are hydrolyzed with difficulty in dilute acid or in alkaline solution at room temperature and hydrogen sulfide is unable to precipitate the metal ion as a sulfide or ligand exchange does not take place with ethylenediaminetetraacetic acid. Each molecular formula of Ni-B determined by the careful elementary analysis indicated two less hydrogens than that calculated from III or the corresponding Ni-A formula. This was evidenced by a mass spectrum for **8** of Ni-B whose parent ion peak appeared at *m/e* 376. The chelate could be derived from **2** of Ni-A whose parent mass number was 378. The structural identity was seen for all Ni-B compounds in their infrared spectra having superimposable absorption patterns on each other in the double-bond region where strong absorptions appear around 1650, 1600, 1590, and 1525 cm^{-1}—slightly different from those in Ni-A.

Significant evidence for the structure determination was found in the hydrolysis of the chelate, as well as in the case of Ni-A. In the experiment for **8**, 2 mol of salicylaldehyde was isolated; therefore the ligand should consist of two salicylidene moieties in the same sense as in Ni-A. The fully conjugated structure VI had been postulated and it was confirmed also by means of pmr spectra.

The spectra were taken for **9** and **10** of Ni-B and they are shown in Figure 2. The spectral patterns are quite simple as a whole, compared to those of Ni-A in Figure 1. A single peak at 1.27 ppm is due to the *tert*-butyl protons (a) in both and a singlet at 2.17 ppm is of the methyl protons (c) in **9** and broad signals between 2.23 and 1.77 ppm are of the cyclohexyl protons (c) in **10**. The azomethine proton (b) signals appear at 7.53 ppm in **9** and at 7.42 ppm in **10**, respectively. The simplicity of these spectral patterns suggests the high symmetry of the Ni-B molecules including the central metal ions and structure VI is definitely supported by the fact that each pmr signal has been reasonably assigned. Thus Ni-B is 1,6-bis(2-hydroxyphenyl)-2,5-diaza-3,4-dialkyl-1,3,5-hexatrienatonickel(II), *i.e.*, a Ni(II) chelate of the bis(salicylidene-1,2-diaminoethylene) derivative.

Square-planar configurations are most probable for both Ni-A and Ni-B because of their diamagnetic characters evidenced by the pmr spectral patterns.

Structures of the Cu(II) and Co(II) Chelates.—The reactions of the oxazines (Ia–Ie) with copper(II) acetate or with cobalt(II) acetate afforded corresponding chelates, both as deep reddish crystals. Unlike the Ni(II) chelates, the Cu(II) and the Co(II) chelates obtained under nitrogen were the same as those obtained in an air atmosphere. The elementary analysis of each one was in good agreement with the case that the Ni-B type structure VI was assumed. The acid hydrolysis which was carried out for **14** gave 2 mol of salicylaldehyde from 1 mol of the chelate.

Mass spectra were taken for **14** and **15** to seek a possibility such as ligand-bridged dimmers. They showed parent ion peaks at *m/e* 381 (^{63}Cu) for **14** and at *m/e* 377 (^{59}Co) for **15**. Each number was equal to the molecular weight calculated from the corresponding structure VI; therefore, any possibilities other than the monomer were excluded. Infrared spectra of the Cu(II) and the Co(II) chelates were all superimposable on each other and on those of Ni-B in the double-bond region where strong absorption appeared around 1650, 1600, 1590, and 1525 cm^{-1}.

In the electronic spectra shown in Figure 3 for the

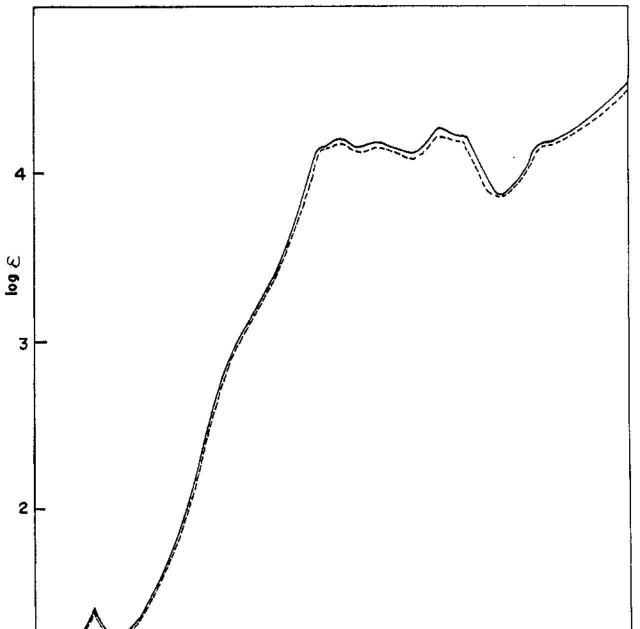

Figure 3.—The electronic spectra of Co(II) chelates in $CHCl_3$: **13**, ----; **15**, —.

Co(II) chelate (**15**), the intense absorptions from 40 $\times$ 10^3 to 15 $\times$ 10^3 cm^{-1} are regarded as resulting mainly from the ligand molecule of a highly conjugated system. There appears a sharp peak at 7.9 $\times$ 10^3 cm^{-1} (log ϵ = 1.26) which is ascribed to d–d transition. Yamada, *et al.*,[5] have suggested in their electronic spectral studies of bis(salicylaldiminato)cobalt(II) that the similar band at 8.3 $\times$ 10^3 cm^{-1} is diagnostic in a discussion of the configuration of Co(II) complexes and is indicative of a low-spin planar Co(II). The magnetic moment for Co(II) complexes is also generally diagnostic of their configurations, and low-spin square-planar complexes show μ_{eff} in the range 2.1–2.9 BM arising from one unpaired electron plus an apparently large orbital contribution.[6] The observed value of μ_{eff} for **15** was 2.44 BM which exactly fell into the above range.

Judging from this evidence, the Co(II) chelates take structure VI having a low-spin square-planar configuration.

The observed magnetic moment for the Cu(II) chelate of **14** was μ_{eff} = 1.79 BM which was almost a spin-only value. This evidence leads to the conclusion that the Cu(II) chelates also take structure VI, although the exact configuration could not be drawn in general from the magnetic moment of copper complexes. Nevertheless, the square-planar configuration is the most probable in this case because of the high planarity of the ligand molecules and the coordination nature of a Cu(II) ion preferably taking a square-planar configuration.

Formation Mechanism of the Chelates.—As for Ni-A, formation of III will be involved as an initial step in the reaction of I with the Ni(II) ion. The proton migration accompanied with simultaneous electron transfer occurred in III from the benzyl methylene to the nearest azomethine carbon atom to form V. Such proton migration has been observed in the study of the hydrolytic cleavage of the oxazines (I), where one of the salicylamine moieties in the isomeric II was removed by the hydrolysis and the benzyl proton in the remaining species migrated to the azomethine carbon atom to give a salicylidene α-amino ketone, which simultaneously underwent trans-Schiffization between the salicylamine and yielded salicylidenesalicylamine as a final product.[1] In the present case, II would be stabilized against the hydrolysis by the formation of the metal chelate III; as a result, the proton migration only occurred giving rise to V.

The formation of Ni-B is definitely due to an air oxidation involving the initial formation of Ni-A, although the detailed mechanism is not clear. The coordinated Ni(II) ion may catalyze the reaction; however, the product contained only oxidized ligand in the sense that hydrogens were removed from the ligand. On the other hand, such dehydrogenation occurred in the absence of oxygen in the Cu(II) and the Co(II) chelates; therefore, the metal ions themselves should participate in the reaction. The change of an oxidation state of the copper from +2 to a lower one was evidenced by a copper mirror formation during the reaction or was realized in an increase of the yield by the reaction of 2 mol of Cu(II) ion in which 1 mol was consumed for the oxidation.

The role of the Co(II) ion could be understood in the same sense as that of the copper ion although no cobalt mirror formation was observed, since the reaction with double amounts of cobalt(II) acetate gave a higher yield. In the reaction of the oxazines with equimolar cobalt(III) acetylacetonate, it is obvious that the change in the oxidation state of the cobalt ion from +3 to +2 accompanies the ligand oxidation.

The formation of the ligand molecules of Ni-B is interesting since such fully conjugated Schiff bases in which the two azomethine nitrogens are bridged by an ethylenic double bond have never been synthesized. Provided diaminoethylene is possible to prepare, this type of Schiff base may be synthesized by the condensation of the diamines with salicylaldehyde; however, such α,β-unsaturated olefinic primary diamines cannot exist in monomeric form. Therefore, the present reaction will be the only way so far to prepare such particular compounds as metal chelate ligands.

Template Reactions.—As reported in the previous paper,[1] the condensation of salicylamine with α-diketones afforded the oxazines under cold conditions or salicylidenesalicylamines under hot conditions. When the reaction had been conducted in the presence of a metal ion, some metal chelates which were identical with those obtained with the corresponding oxazines were isolated directly without oxazine formation. It is obvious that the coordination sphere of the metal ion played a role as a template in this case. Further, the template reaction proceeded even in such cases where the oxazines could not be isolated in the absence of the metal ion. The metal chelates **6** (Ni-A), **11** (Ni-B), **22** (Cu), and **23** (Co) were possible to prepare in this way. No oxazine was obtained with 5-chlorosalicylamine and 2,3-butanedione recovering the starting materials, while the template reaction did proceed with the Ni(II) ion in the absence and in the presence of air to give **6** and **11**, respectively, and with the Co(II) ion to give **23**. The reaction of salicylamine with 2,3-pentanedione also gave no oxazine due to the predominant formation of salicylidenesalicylamine; however, the Cu(II) chelate (**22**) was obtained by the template reaction. The structures of these metal chelates were confirmed, as listed in Tables I and II, by their infrared spectra which exhibited superimposable patterns with the authentic chelates whose structures had been confirmed as described above.

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