Cobalt(II) Complexes of Schiff Bases Derived from Salicylaldehyde and Aromatic Amines[1]

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The preparation and the configuration of cobalt complexes of Schiff bases derived from salicylaldehyde and alkyl amines have been described in previous papers.[2] On the other hand, there have also been a comparatively large number of papers available about cobalt complexes of *N*-aryl-salicylideneimines.[3] As a conclusion of the previous studies, it has generally been postulated that quadri-co-ordinate cobalt(II) complexes do not exist with Schiff bases which have substituents on the ortho-carbon atom in Fig. 1. In fact, bis-(*N*-*o*-methoxyphenyl-salicylideneiminato)-cobalt(II) was synthesized, but its formation was regarded as due to stabilization through the sexa-co-ordination attained by the additional linkage of the oxygen atoms of the methoxy groups with the cobalt(II) ion.[3] The present authors have recently succeeded in preparing several cobalt(II) complexes with Schiff bases which have substituents on the *o*-carbon atom. In the present paper the syntheses of bis(*N*-aryl-salicylideneiminato)cobalt(II) complexes will be described, and the configurations of these complexes will be examined on the basis of the results of the preceding papers.

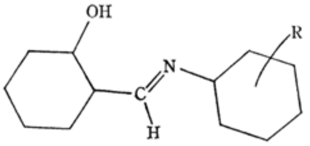

Fig. 1. *N*-Aryl-salicylideneimine.

Experimental

Meterials. — Salicylideneiminato-cobalt(II) complexes with *N*-*o*-substituted aryl groups were generally prepared in the following way. A yellow powder of $Co(sal)_2\cdot 2H_2O$ was mixed with an excess (1.5 to 4.5 times the theoretical amount) of one of the amines to yield orange-colored paste; the notation "*sal*" denotes an anion which is formed when a molecule of salicylaldehyde loses a proton. A suitable organic solvent was boiled in another flask until the flask was filled with its vapor above the liquid phase. The paste of the mixture was then placed into the flask, and immediately the flask was closed tightly. The reaction was continued at a temperature just below the boiling point of the solvent. The period required for the reaction varied depending upon the amine used. After the reaction was over, the solution was cooled very slowly. The solution underwent oxidation when the temperature was appreciably higher than room temperature.

For the preparation of bis(*N*-*o*-tolylsalicylideneiminato)cobalt(II), $Co(sal)_2\cdot 2H_2O$ (1.0 g.) and *o*-toluidine (3.0 g.) were used as the starting materials and ethanol (30 ml.) as a solvent. The general method described above was followed. After the flask had been closed tightly, the reaction was continued for about fifteen minutes at 70°C to 75°C; then the solution was allowed to stand until its temperature went down to room temperature. After it had been kept for a day or two at −15°C, the compound was obtained in deep-red, hexagonal plates.

Found: C, 69.9; H, 5.08; N, 5.92. Calcd. for $C_{28}H_{24}N_2O_2Co$: C, 70.2; H, 5.05; N, 5.84%.

For the preparation of bis(*N*-*o*, *m*-xylidyl-salicylideneiminato)cobalt(II), $Co(sal)_2\cdot 2H_2O$(1.0 g.) and *o*, *m*-xylidine (1.2 ml.) were used as the starting materials and methanol (22 ml.) as a solvent. After the flask had been closed tightly, the reaction was continued for about four hours at 60°C. Then the solution was allowed to cool slowly to −15°C. After the solution had been kept at −15°C for three days, the deep-red needles which separated out were collected.

Found: C, 70.7; H, 5.53; N, 5.86. Calcd. for $C_{30}H_{28}N_2O_2Co$: C, 71.0; H, 5.56; N, 5.52%.

For the preparation of bis(*N*-*o*, *o'*-xylidyl-salicylideneiminato)cobalt(II), $Co(sal)_2\cdot 2H_2O$ (1.0 g.) and *o*, *o'*-xylidine (1.4 g.) were used as the starting materials and methanol (40 ml.) as a solvent. The reaction was continued for several hours at 60°C. Then the orange powder of $Co(sal)_2\cdot 2H_2O$ was completely dissolved, giving a bright red solution. The reaction was then continued for several more hours until the red crystals started to separate out. Then the solution was cooled to 15°C, and the red crystals of the product were collected. The compound was also synthesized by the reaction of

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[1] A brief account has previously been published as a Short Communication. H. Nishikawa and S. Yamada, This Bulletin, 35, 1430 (1962).

[2] a) H. Nishikawa and S. Yamada, This Bulletin, 37, 8 (1964); H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, 17b, 78 (1962); *Z. anorg. u. allgem. Chem.*, 316, 278 (1962); S. Yamada and H. Nishikawa, This Bulletin, 36, 755 (1963), etc. b) L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, *J. Am. Chem. Soc.*, 85, 411 (1963); L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, ibid., 84, 3246 (1962), etc.

[3] B. O. West, *Nature*, 173, 1187 (1954); *J. Chem. Soc.*, 1952, 3115; ibid., 1960, 4944; ibid., 1962, 1374, etc.

theoretical amounts of cobalt(II) acetate tetrahydrate, *o, o'*-xylidine, salicylaldehyde and sodium hydrogencarbonate in ethanol, stirring the solution for about four hours at room temperature. Recrystallization from methanol yielded pure crystals of the product.

Found: C, 71.1; H, 5.52; N, 5.22. Calcd. for $C_{30}H_{28}N_2O_2Co$: C, 71.0; H, 5.56; N, 5.52%.

For the preparation of bis(*N*-α-naphthyl-salicylideneiminato)cobalt(II), Co(*sal*)$_2$·2H_2O (1.0 g.) and α-naphthyl amine were used as the starting materials and methanol as a solvent. After the flask had been closed tightly, the reaction was continued. As the orange powder of Co(*sal*)$_2$·2H_2O was dissolved, red crystals started to separate out. The flask was cooled very slowly to room temperature.

Found: C, 73.6; H, 4.36; N, 4.96. Calcd. for $C_{34}H_{24}N_2O_2Co$; C, 74.0; H, 4.39; N, 5.08%.

For the preparation of bis(*N-o*-chlorophenyl-salicylideneiminato)cobalt(II), Co(*sal*)$_2$·2H_2O (1.0 g.) and *o*-chloroaniline (3.3 g.) were used as the starting materials and ethanol (45 ml.) as a solvent. After the flask had been closed, the reaction was continued for four hours at 70°C to 75°C. The flask was cooled to room temperature, and the solution was kept at −15°C for one day, A brownish black mass was obtained. By extracting the mass with pyridine, orange-yellow crystals of Co(O·C_6H_4·CH : N·*o*-Cl·C_6H_4)$_2$·2*py* were obtained.

Found: C, 63.5; H, 4.31; N, 8.51; Cl, 10.21. Calcd. for $C_{36}H_{28}N_4O_2Cl_2Co$: C, 63.7; H, 4.16; N, 8.26; Cl, 10.5%.

After the pyridine adduct had been left at 70°C in vacuo for several hours, an orange-yellow powder of bis(*N-o*-chlorophenyl-salicylideneiminato)cobalt(II) was obtained.

Found: C, 60.3; H, 3.61; N, 5.22. Calcd. for $C_{26}H_{18}N_2O_2Cl_2Co$: C, 60.0; H, 3.49; N, 5.38%.

For the preparation of bis(*o, p, o'*-trichlorophenyl-salicylideneiminato)cobalt(II), a theoretical amount of potassium metal (0.8 g.) dissolved in ethanol (10 ml.) was stirred into a solution of cobalt acetate tetrahydrate (2.5 g.) and *N-o, p, o'*-trichlorophenyl-salicylideneimine (6.2 g.) in lukewarm ethanol (25 ml.). The vessel was then tightly closed and left to stand for a day at −15°C. The orange powder which sparated out was collected by filtration and washed with ether. The compound was soluble in chloroform and benzene.

Found: C, 47.5; H, 2.45; N, 4.15. Calcd. for $C_{26}H_{14}N_2O_2Cl_6Co$: C, 47.5; H, 2.14; N, 4.26%.

For the preparation of bis(*o, p, o'*-tribromophenyl-salicylideneiminato)cobalt(II), salicylaldehyde (4.9 g.) and tribromoaniline (13.2 g.) were refluxed for two hours in 150 ml. of amyl alcohol. Then piperidine (4.0 g.) and cobalt acetate tetrahydrate (4.9 g.) were added to the solution, and it was refluxed for about two hours. About 100 ml. of toluene was then added to the solution, and it was refluxed for about ten minutes. After the solution had been gradually evaporated at about 100°C to a volume of about 70 to 80 ml., it was cooled and allowed to stand at −15°C for a few days. The compound was obtained as an orange-red crystalline powder, which was then washed with benzene and chloroform.

Found: C, 33.8; H, 1.66; N, 3.13. Calcd. for $C_{26}H_{14}N_2O_2Br_6Co$: C, 33.6; H, 1.52; N, 3.01%.

Bis(*N*-phenyl-salicylideneiminato)cobalt(II), bis(*N-m*-substituted aryl-salicylideneiminato)cobalt(II) and bis(*N-p*-substituted aryl-salicylideneiminato)-cobalt(II) were prepared by the method of West.[3)]

All these compounds in the solid state are stable to the atmosphere.

Measurements.—The electronic absorption spectra of the compounds in soltuion were determined with a Beckman DU spectrophotometer in the near-infrared, visible and ultraviolet regions. Beer's law was generally obeyed in the concentration range between 10^{-3} and 10^{-5} mol./l., except for the trichlorophenyl derivative of cobalt(II). Pyridine for a solvent is purified by distillation after having been dried with potassium carbonate.

Results and Discussion

Bis(*N*-aryl-salicylideneiminato)cobalt(II).—It seems to be significant that bis(*N-o*-substituted aryl-salicylideneiminato)cobalt(II) complexes were prepared as crystals in this work. It has generally been believed that, because of the serious strain to the tetrahedral co-ordination around the cobalt(II) ion, quadri-co-ordinate cobalt(II) complexes can not be formed with the Schiff bases which are shown as having a substituent on the ortho-carbon atom in Fig. 1. One success in preparing these compounds, however, shows that this is definitely not the case. The preparation of bis(*N-o*-tolyl-salicyli-

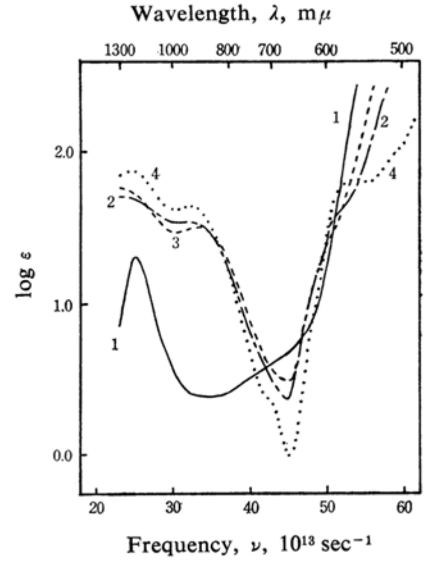

Fig. 2. Electronic absorption spectra of: 1, Co(O·C_6H_4·CH : N·CH_2CH_2N : CH·C_6H_4·O) in chloroform (——); 2, Co(O·C_6H_4·CH : N·*o*-CH_3·C_6H_4)$_2$ in benzene (—·—); 3, Co(O·C_6H_4·CH : N·*p*-CH_3·C_6H_4)$_2$ in benzene (----); 4, Co(O·C_6H_4·CH : N·*t*-C_4H_9)$_2$ in benzene (······).

deneiminato)cobalt(II) has also been announced quite recently by West.

As has been shown previously,[2)] the electronic absorption spectrum of the cobalt(II) complex depends upon the configuration of the complex, and it may be used diagnostically in the discussion of the configuration of the cobalt(II) complexes. For substituents such as methyl and chloro groups, bis(*N*-*o*-substituted arylsalicylideneiminato)cobalt(II) complexes in non-co-ordinating solvents (Figs. 2 and 3) all show similar absorption spectra which are different from the spectra characteristic of the planar cobalt(II) complexes,[4)] but which bear a close resemblance to the spectra regarded as being characteristic of quadri-co-ordinate, tetrahedral cobalt(II) complexes.[2)] It may, therefore, be concluded that all these cobalt(II) complexes take a tetrahedral co-ordination around the cobalt(II) ion. The same configuration may be concluded for the trichlorophenyl- and the tribromophenyl- complexes in non-co-ordinating solvents (Fig. 3), although these complexes were not stable enough for us to determine the exact absorption spectra in solution. When a group attached to N is α-naphthyl, the situation is similar to that with the corresponding complex with *o*-substituted phenyl for R; the comparison of the spectra, which are shown in Fig. 2, indicates that bis(*N*-α-naphthyl-salicylideneiminato)-cobalt(II) also has a tetrahedral co-ordination.

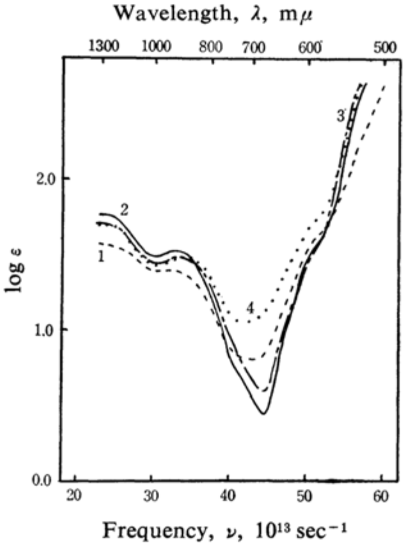

Fig. 3. Electronic absorption spectra of $Co(O\cdot C_6H_4\cdot CH:N\cdot R)_2$ in benzene: 1, R=*o*-Cl$\cdot C_6H_4$ (----); 2, R=*m*-$CH_3\cdot C_6H_4$ (——); 3, R=*p*-Cl$\cdot C_6H_4$ (—·—); 4, R=*m*-Cl$\cdot C_6H_4$ (……).

Bis(*N*-*m*- and bis(*N*-*p*-substituted aryl-salicylideneiminato)cobalt(II) complexes were concluded previously from magnetic measurements to have a tetrahedral configuration.[3)] The electronic absorption spectra examined in this work (Fig. 3) also support this conclusion. The absorption bands at about 24×10^{13} sec^{-1} may be tentatively assigned as a $^4A_2\rightarrow{}^4T_1(F)$ transition in the notation of the T_d field symmetry.

It may be concluded that the co-ordination around the cobalt(II) ion in these compounds is tetrahedral, whether the substituent is on the *o*-, *m*- or *p*-position. It should be noted that the cobalt(II) complexes of the *o*,*o*′-disubstituted and of the mono-substituted ligands have a tetrahedral configuration, while the corresponding compounds of copper(II) and nickel(II) are known to take a planar co-ordination. Thus, it is again found that, in general, a tetrahedral configuration is more favorable for the cobalt(II) complex than for the copper(II) and the nickel(II) complexes, in agreement with the conclusion reached by the simple crystal field theory.

Bis(*N*-*o*-methoxyphenyl-salicylideneiminato)-cobalt(II) shows the ligand field bands at about 33 and 20×10^{13} sec^{-1}, as may be seen in Fig. 4. These bands bear a resemblance to those of the other cobalt(II) compounds of the Schiff bases prepared in the present work. A slight difference between the *o*- and the *p*-derivatives, however, is seen in the ligand field bands of the complexes, the bands of the *o*-methoxy-derivative, for instance, being broader

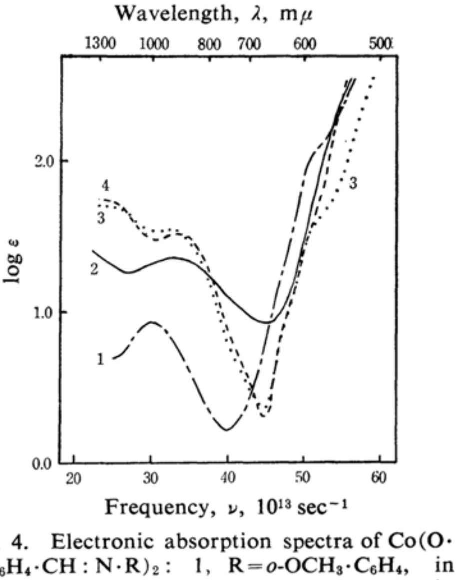

Fig. 4. Electronic absorption spectra of $Co(O\cdot C_6H_4\cdot CH:N\cdot R)_2$: 1, R=*o*-$OCH_3\cdot C_6H_4$, in pyridine (—·—); 2, R=*o*-$OCH_3\cdot C_6H_4$, in chloroform (——); 3, R=*o*-$CH_3\cdot C_6H_4$, in benzene (……); 4, R=*p*-$OCH_3\cdot C_6H_4$, in benzene (----).

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4) H. Nishikawa and S. Yamada, This Bulletin, 37, 8 (1964).

than those of bis(*N*-*p*-methoxyphenyl- as well as those of bis(*N*-*o*-tolyl-salicylideneiminato)-cobalt(II). This fact suggests that the configuration of the cobalt(II) complex with the *o*-methoxyphenyl group is somewhat anomalous compared with those of the other compounds of a similar type, in agreement with the view of West,[3] who postulated a weak interaction between the oxygen atom of the methoxy group and the central cobalt(II) ion. Since the absorption spectrum of the compound, however, is quite different from that of a typical sexa-co-ordinate cobalt(II) compound, the interaction between the oxygen atom and the cobalt(II) ion may not be very strong.

The Configuration of Bis(*N*-aryl-salicylideneiminato)cobalt(II) Complexes in Pyridine. — When R represents *m*- and *p*-methyl radicals, the steric condition does not greatly differ from that of the corresponding phenyl compound. The absorption spectra of these complexes (Fig. 5) clearly show that their configurations, which are all tetrahedral in non-donor solvents, are sexa-co-ordinate, octahedral in pyridine.[5] The absorption bands at about 30 and 51.5×10^{13} sec^{-1} may be tentatively identified as $^4T_1\rightarrow{}^4T_2$ and $^4T_1\rightarrow{}^4T_1(P)$ transitions respectively. Judging from the steric condition, it is quite difficult for the two molecules of pyridine to be co-ordinated to the central cobalt(II) ion in the bis(*N*-*o*,*o*'-xylidyl-salicylideneiminato) complex to complete a sexa-co-ordination around the cobalt(II) ion. The absorption spectra of these cobalt(II) complexes in pyridine (Fig. 6) differ definitely, though not greatly, from the spectra of the tetrahedral cobalt(II) complexes. The presence of the sexa-co-ordinate pyridine adduct of this complex may be excluded since (1) the steric factor is quite unfavorable for the octahedral configuration around the cobalt(II) ion, and (2) the absorption curve shows no clear peak in the frequency region, where the octahedral pyridine adduct is expected to absorb. It is, therefore, most likely that the quinque-co-ordinate complex with one molecule of pyridine is present in the pyridine solution. Thus, the inspection of the absorption curve seems to indicate that in the pyridine solution there is an equilibrium consisting of the quadri-co-ordinate, the tetrahedral and the quinque-co-ordinate complexes.[6] Evidence for the existence of the quinque-co-ordinate complex may be afforded by the isolation of the possibly

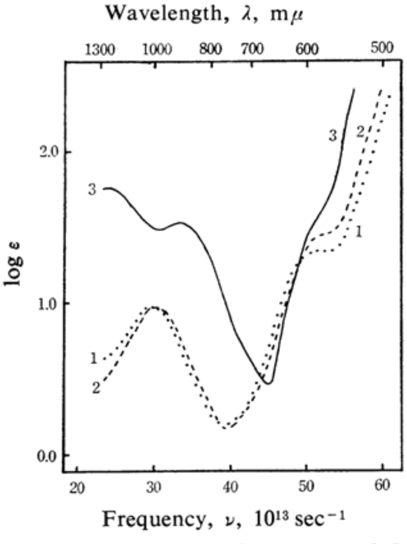

Fig. 5. Electronic absorption spectra of Co(O·C_6H_4·CH : N·R)$_2$: 1, R=*o*-CH_3·C_6H_4, in pyridine (……); 2, R=*m*-CH_3·C_6H_4, in pyridine (----); 3, R=*m*-CH_3·C_6H_4, in benzene (——).

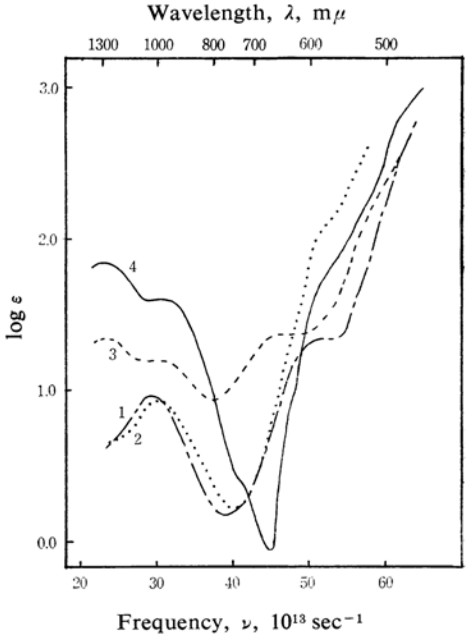

Fig. 6. Electronic absorption spectra of Co(O·C_6H_4·CH : N·R)$_2$: 1, R=*o*-CH_3·C_6H_4, in pyridine (—-—); 2, R=*o*-OCH_3·C_6H_4, in pyridine (……); 3, R=*o*, *o*'-$(CH_3)_2$·C_6H_3, in pyridine (----); 4, R=*o*, *o*'-$(CH_3)_2$·C_6H_3, in benzene (——).

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[5] About the *N*-phenyl-complex of cobalt(II), the same result was reported previously; L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

[6] Quite recently, Sacconi and Ciampolini (private communication) studied the equilibrium between bis-(salicylaldehyde) - *N*, *N* - disubstituted polymethylenediiminato cobalt(II) complexes and their pyridine adducts in solution, and found that, in some cases, the first step of the equilibrium was that between the original tetrahedral complex and the quinque-co-ordinate cobalt(II) adduct with one pyridine molecule.

quinque-co-ordinate adduct of the *o,o'*-dimethyl complexes with one pyridine molecule, which is quite a different color from that of the parent compound.[7] The reflection spectrum of the compound is obviously different from any of the known spectra of the tetrahedral, square-planar and octahedral complexes of cobalt(II).[7]

The adducts with two pyridine molecules were generally isolated for the corresponding cobalt(II) complexes of most *N*-aryl-substituted Schiff bases and show absorption bands which are considered to be characteristic of the octahedral complexes.

When a group attached to N is an *o*-methoxyphenyl radical, the absorption spectrum of the cobalt(II) complex in pyridine (Fig. 4) is quite different from that in chloroform; it shows the band at $30\times10^{13}\,\mathrm{sec}^{-1}$ ($\log\varepsilon$ about 0.9) which is considered to be the ligand field band of the sexa-co-ordinated cobalt(II) complex formed by the co-ordination of two molecules of pyridine.[8] It is most likely, therefore, that the weak bond originally present between the oxygen atom of the methoxy group and the cobalt(II) ion is broken in pyridine, so that the molecules of pyridine are combined with the cobalt(II) ion to yield another sexa-co-ordinate cobalt(II) complex.

Summary

Bis(*N*-aryl-salicylideneiminato)cobalt(II) complexes, including several new compounds, have been prepared and their configurations examined. These cobalt(II) compounds have been concluded, from their electronic spectra, to have a tetrahedral configuration around the cobalt(II) ion. All these compounds in pyridine have been concluded to take an octahedral configuration with the exception of the *N-o,o'*-disubstituted cobalt(II) compounds.

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

[8] The electronic spectrum of the *o*-methoxyphenyl complex in chloroform in Fig. 4 is essentially the same as the spectrum of the same complex in benzene.