Planar Quadri-co-ordinate Complexes of Cobalt(II) with Schiff Bases Derived from Salicylaldehyde

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The chemistry of transition-metal complexes with Schiff bases derived from salicylaldehyde is considered to involve a number of interesting problems of fundamental importance in the field of co-ordination chemistry.[1-3] The copper(II) and nickel(II) compounds of this type have been studied in some detail, but there have been very few systematic studies of cobalt(II)-complexes with *N*-alkylsalicylideneiminate ions. Thus, the configuration of quadri-co-ordinate cobalt(II)-complexes of this kind was in dispute when the present study was started. There are some cobalt(II)-complexes in which the steric requirements alone determine the configuration of the complex, allowing only one of two possibilities, that is, a planar or a tetrahedral co-ordination. As a step to the elucidation of the structure of cobalt(II)-complexes with Schiff bases, the present paper is concerned with those compounds whose structure is necessarily planar because of the steric conditions imposed by the ligands, and with the determination of the main characteristics of their spectroscopic properties. The electronic spectra of the planar cobalt(II)-complexes have never been unanimously characterized; it is thought that their establishment will be useful for the discussion of the structure of, and the chemical bond involved in, cobalt(II)-complexes.

Experimental

Materials. — *Bis(salicylaldehyde)ethylenediiminatocobalt(II)*[4] (Fig. 1, A) was prepared previously[5] by adding an aqueous solution of cobalt(II) acetate to an ethanolic solution of bis(salicylaldehyde)-ethylenediimine under reduced pressure. The crystals of the compound obtained by this method, however, are generally so small that they are very susceptible to oxygenation. In the present work, a different method was devised for preparation of the compound in larger cystals, which were bound to be more inert in the atmosphere. A suspension of bis(salicylaldehyde)cobalt(II) dihydrate (2.0 g.) in methanol (400 ml.) was boiled in a flask. While this was boiling and while the vapor of methanol filled the flask, a theoretical amount of ethylenediamine was added to the orange-colored solution; then the flask was closed tightly. When the mixture was kept at room temperature for a few hours, needle-like crystals first started to separate out; these were soon changed, in the solution in the absence of oxygen, into dark-violet, prism-like crystals, which were finally collected. The nature of the red crystals which separated at first and which then disappeared was not characterized in the present study. The dark-violet crystals obtained according to this method are hardly oxygenated at all, even when filtered in the air. They are slightly soluble in chloroform and benzene.

Found: C, 59.3; H, 4.36; N, 8.90. Calcd. for $C_{16}H_{14}O_2N_2Co$: C, 59.1; H, 4.34; N, 8.61%.

Bis(salicylaldehyde)propylenediiminatocobalt(II) (Fig. 1, B) was prepared as reddish-brown, needle-like crystals by a new method similar to that for "salcomine" which was devised by the present authors. The crystals, which are readily oxygenated in the atmosphere, are slighty soluble in ethanol, chloroform and benzene.

Found: C, 59.4; H, 4.90; N, 8.00. Calcd. for $C_{17}H_{16}O_2N_2Co$: C, 61.2; H, 5.13; N, 7.93%.

Bis(salicylaldehyde)-α, α'-dimethylethylenediiminatocobalt(II) (Fig. 1, C) was previously reported by Diehl.[6] In the present work, a different method was devised. Under reduced pressure, bis(salicylaldehyde)-cobalt(II) dihydrate and a slight excess of α, α'-dimethylethylenediamine were reacted in a water-ethanol mixture for several minutes. Then the solution was evaporated in vacuo to give an orange, crystalline powder. The micro-crystals, which are stable in the atmosphere, are soluble in common organic solvents.

Found: C, 60.5; H, 5.45; N, 7.47. Calcd. for $C_{18}H_{18}O_2N_2Co$: C, 61.2; H, 5.13; N, 7.93%.

Bis(salicylaldehyde)-α, α'-diphenylethylenediiminatocobalt(II) (Fig. 1, D) has not been reported yet. In the present study, this compound was synthesized from bis(salicylaldehyde)cobalt(II) dihydrate and α, α'-diphenylethylenediamine according to a method similar to that used for bis(salicylaldehyde)-α, α'-dimethylethylenediiminatocobalt(II). Recrystallization of the crude product from chloroform yielded pure, red crystals, which are quite stable in the atmosphere. These crystals are soluble in ethanol,

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1) H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962); *Z. anorg. u. allgem. Chem.*, **316**, 278 (1962); H. Nishikawa and S. Yamada, This Bulletin, **35**, 1430 (1962); S. Yamada and H. Nishikawa, ibid., **36**, 755 (1963), etc.

2) B. O. West, *J. Chem. Soc.*, **1962**, 1374; ibid., **1960**, 4944; *Nature*, **173**, 1187 (1954), etc.

3) L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962); L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, ibid., **85**, 411 (1963), etc.

4) This compound is abbreviated "salcomine."

5) P. Pfeiffer, E. Breith, L. Lübbe and T. Tsumaki, *Ann.*, **503**, 84 (1933).

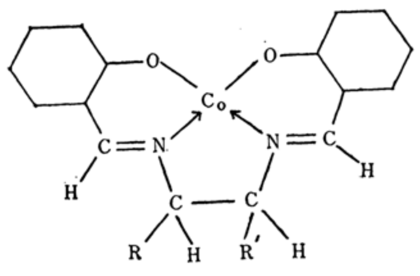

Fig. 1. Bis(salicylaldehyde)ethylenediiminatocobalt(II) and related compounds.
A, R=R'=H; B, R=H, R'=CH_3; C, R=R'=CH_3; D, R=R'=C_6H_5.

chloroform and benzene, and they are stable in solution as well as in the solid state.

Found: C, 71.6; H, 4.99; N, 5.47. Calcd. for $C_{28}H_{22}N_2O_2Co$: C, 70.4; H, 4.64; N, 5.86%.

Bis(salicylaldoximato)cobalt(II) was prepared by a new method, one invented for the present work in order to obtain crystals of a larger size by avoiding undesirable oxygenation during the process. Prior to the synthesis, the fiask was evacuated, and it was eventually filled with ethanol vapor. Cobalt(II) chloride and salicylaldoxime were dissolved in warm ethanol in the molar ratio of 1:2.2, and a methanolic solution of lithium methylate (2.0 mol.) was added drop by drop to the solution. Red-brown crystals separated out immediately, and they were collected. The crystals obtained are slightly soluble in common organic solvents.

Found: C, 50.7; H, 3.59; N, 8.04. Calcd. for $C_{14}H_{12}N_2O_4Co$: C, 50.8; H, 3.65; N, 8.46%.

Bis(salicylaldiminato)cobalt(II) was prepared by the following two methods: (i) Bis(salicylaldehyde)cobalt(II) dihydrate (2.0 g.) was suspended in 200 ml. of ethanol in a flask at 60~65°C. A concentrated aqueous ammonia (9 ml.) was added to the solution in the flask which was evacuated, and the reaction mixture was kept at this temperature for about one and a half hours to give orange, plate-like crystals. The crystals were filtered, washed with a mixture of a concentrated aqueous ammonia and methanol, and dried in vacuo. (ii) Bis(salicylaldehyde)cobalt(II) dihydrate (2.5 g.), ammonium chloride (2.5 g.) and methanol (100 ml.) were placed in a flask, which was evacuated until the solution in it started boilig.

Then the flask was closed and warmed to 65°C while being stirred, and lithium methylate prepared from lithium metal (0.28 g.) and methanol (20 ml.) was added drop by drop into the flask. Orange, plate-like crystals separated out immediately; they were filtered while hot, washed with a mixture of concentrated aqueous ammonia and methanol, and dried in vacuo.

The crystals are readily soluble in pyridine, but insoluble in other common organic solvents.

Found: C, 56.0; H, 4.05; N, 9.38. Calcd. for $C_{14}H_{12}N_2O_2Co$: C, 56.2; H, 4.04; N, 9.36%.

The crystals prepared by the above-described methods are obviously different from those reported previously. Fomerly Endo⁷⁾ claimed to have isolated bis(salicylaldiminato)cobalt(II) dihydrate from hydrosalicylamide and cobalt(II) acetate. Our experiments using his procedures yielded a substance with the same properties as those described in the literature. The substance, however, gave an analytical value for nitrogen, an appreciable deviation from the formula of bis(salicylaldiminato)-cobalt(II) or its hydrate. Moreover, observation under a microscope indicates that the product consists of two kinds of crystals. It is likely that a mixture is obtained by this procedure. The most remarkable difference seems to be that the product obtained by the Endo's method was reported to be stable in boiling chloroform, whereas the product obtained by the method reported here was quite sensitive to air.

Measurements.—The electronic absorption spectra of the compounds in solution were determined with a Beckman DU spectrophotometer. Since all the compounds are more or less sensitive to oxygen in the air, the measurements were carried out in a nitrogen atmosphere. Examination was made after every measurement to see whether or not any change occurred in the solution. In general, Beer's law was obeyed in the concentration range of the present measurements, which varied between 10^{-2} and 10^{-5} mol./l.

Results and Discussion

Bis(salicylaldehyde)ethylenediiminatocobalt(II) and Its Derivatives.—Judging from the steric requirement of the ligand (Fig. 1, A), bis(salicylaldehyde)ethylenediiminatocobalt(II) is considered to have a quadri-co-ordinate, planar complex of the *cis*-$[Co(N)_2(O)_2]$ type. The visible and ultraviolet spectrum of "salcomine" in solution has previously been reported, but the measurement did not cover the whole region of the ligand field bands.⁸⁾ In the present study, therefore, the measurements were carried out in the atmosphere of nitrogen and were extended to a much lower frequency region than that previously reported. The results of the measurements are shown in Fig. 2. In the region of the higher frequency, there appear intense absorption bands; these are regarded as resulting mainly from the ligand group in the complex. These absorption bands, however, do not extend beyond $60\times10^{13}sec^{-1}$ (500 mμ), so that a considerable part of the ligand field band region is left uncovered. In the lower frequency region, the main features of the ligand field bands of "salcomine" are definitely different from those of cobalt(II)-complexes with a sexa-co-ordinate octahedral

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6) H. Diehl and T. S. Chao, *Iowa State Coll. J. Sc.*, 22, 126 (1947).

7) J. Endo, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaisi*), 65, 428 (1944).

8) R. Tsuchida and T. Tsumaki, This Bulletin, 13, 527 (1938).

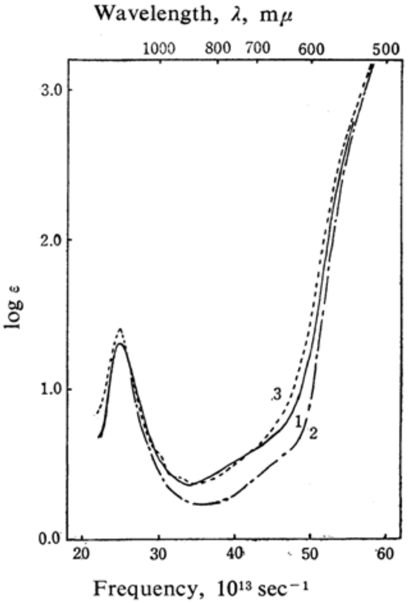

Fig. 2. Visible and near-infrared absorption spectra of "salcomine" and related compounds in chlorofom.
1, $Co(O\cdot C_6H_4\cdot CH:N\cdot CH_2\cdot CH_2\cdot N:CH\cdot C_6H_4\cdot O)$, (salcomine); 2, $Co(O\cdot C_6H_4\cdot CH:N\cdot CH(CH_3)\cdot CH(CH_3)\cdot N:CH\cdot C_6H_4\cdot O)$; 3, $Co(O\cdot C_6H_4\cdot CH:N\cdot CH(C_6H_5)\cdot CH(C_6H_5)\cdot N:CH\cdot C_6H_4\cdot O)$.

or a quadri-co-ordinate tetrahedral configuration. Thus, the spectrum of "salcomine," which has a sharp peak at about 25×10^{13} sec^{-1} (1200 mμ), may be considered to represent the main features characteristic of cobalt(II)-complexes with a planar configuration.

Bis(salicylaldehyde)propylenediiminatocobalt(II) is regarded, on the basis of the steric condition (Fig. 1), as taking a quadri-co-ordinate, cis-planar configuration. The ligand field bands (Fig. 3) of bis(salicylaldehyde)-propylenediiminatocobalt(II) are quite similar to those of "salcomine," both show a sharp absorption peak at about 25×10^{13} sec^{-1} (1200 mμ).

Bis(salicylaldehyde)-α, α'-disubstituted ethylenediiminatocobalt(II) complexes (Fig. 1) are also considered, on the basis of the steric condition of the ligands, to take a planar co-ordination around the cobalt(II) ion. Thus, compouds C and D (Fig. 1) both show spectra quite similar to that of "salcomine," as is shown in Fig. 2. The sharp peaks in the near-infrared region of the complexes shown in Fig. 1 do not differ much from one another (Table I).

It is of significance that the quadri-co-ordinate cobalt(II)-complexes with a planar configuration, examined in the present study, exhibit characteristic ligand field bands, with a sharp peak at about 25×10^{13} sec^{-1} (1200 mμ). Since this is remarkably different from that which is observed for sexa-co-ordinate octahedral or quadri-co-ordinate tetraherdal complexes of cobalt(II), this difference may be diagnostic in the discussion of the configuration of cobalt(II)-complexes.

TABLE I. LIGAND FIELD ABSORPTION BANDS OF BIS(SALICYLALDEHYDE)ETHYLENEDIIMINATO-COBALT(II) AND RELATED COMPLEXES WITH A PLANAR CONFIGURATION

Compound	ν	$\Delta\nu$	log ε
Compound I	25.1	3.6	1.31
Compound II	24.9	3.9	1.31
Compound III	25.1	3.3	1.31
Compound IV	24.9	3.2	1.40
Bis(sal. aldoxim.)-cobalt(II)	28.6	4.0	(0.99)
Bis(sal. aldimin.)-cobalt(II)	24.9	1.6	(1.49)

ν: 10^{13} sec^{-1}; $\Delta\nu$: half width, 10^{13} sec^{-1}

It is also characteristic that the oscillator strength of this sharp peak in the near-infrared region is very small. Although an unambiguous assignment of the band is difficult at the time, the quite small oscillator strength of the band seems to indicate that this peak may be ascribed to a spin-forbidden d-d transition. On the basis of the energy level diagram provided by Cotton and Holm,[9] the peak may tentatively be ascribed to an electronic transition from $^2B_{2g}$ to $^4A_{2g}$ or ^4E_g.

The Configuration of Bis(salicylaldoximato)- and Bis(salicylaldiminato)-cobalt(II).—The co-ordination around the cobalt(II) ion in bis-(salicylaldoximato)-cobalt(II) is either planar or tetrahedral. From the magnetic moment of 2.6 B. M. for the compound in the solid state,[10] it was formerly assumed that the compound had a planar configuration.[11] This compound is exceedingly susceptible to oxidation, and a specimen obtained by the conventional method of preparation often contains oxygen molecules absorbed from the atmosphere.[12] It is not quite certain whether or not, in the former studies of the magnetic moment, due care was exercised in this respect; reexamination of the problem, preferably using evidence of another sort, was thought to be desirable. In the present work, the pure specimen of bis(salicylaldoximato)cobalt(II) has been prepared with the utmost care to prevent the undesirable oxygenation, and the

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9) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

10) D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. W.*, **74**, 475 (1941).

11) B. M. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1954**, 12.

12) B. O. West, ibid., **1952**, 3120, 3115.

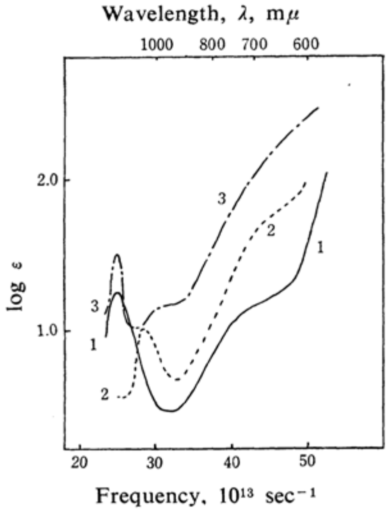

Fig. 3. Visible and near-infrared absorption spectra.
1, $Co(O\cdot C_6H_4\cdot CH:N\cdot CH(CH_3)\cdot CH_2\cdot N:CH\cdot C_6H_4\cdot O)$ in ethanol; 2, $Co(O\cdot C_6H_4\cdot CH:N\cdot OH)_2$ in chloroform; 3, $Co(O\cdot C_6H_4\cdot CH:N\cdot H)_2$ in ethyl methyl ketone.

spectrum of the compound in solution has also been determined in an inert atmosphere. The qualitative spectrum thus determined is shown in Fig. 3. In spite of the great care paid to the determination of the spectrum, a slight oxidation is noticeable in the determined spectrum, which shows an inflation at about 45×10^{13} sec^{-1}. The spectrum, however, is regarded as being accurate enough for the purpose and the nature of the present discussion. The spectrum has a sharp peak, at about 28.4×10^{13} sec^{-1}, which is characteristic of the quadri-co-ordinate square-planar complex of cobalt(II). It may, therefore, be concluded that bis(salicylaldoximato)cobalt(II) has a quadri-co-ordinate planar configuration around the cobalt(II) ion. A comparison of the absorption maximum of the sharp peak in the near-infrared region reveals that the ligand field of the salicylaldoximate ion in the planar cobalt(II)-complex is stronger than that of salicylaldiminate or bis(salicylaldeyde)ethylenediiminate.

It will be shown in forthcoming papers that, with *N*-alkyl- and *N*-aryl-salicylideneimine, most quadri-co-ordinate cobalt(II)-complexes take a tetrahedral configuration, unless the steric condition of the ligands demands a planar co-ordination. It is to be noted that bis(salicylaldoximato)- and bis(salicylideneiminato)-cobalt(II) take a quadri-co-ordinate planar configuration; this is especially noteworthy in view of the fact that these ligands, which are similar in their bonding ability to salicylaldoximate or bis(salicylaldehyde)ethylenediiminate, except for the steric factor, do not necessarily demand a planar configuration for cobalt(II).

One of the necessary conditions for the cobalt(II)-complex to take a planar co-ordination is that the field produced by the ligands in the complex be stronger than a certain threshold value, below which the complex is assumed to take a tetrahedral co-ordination with the ligands. Another cause for the formation of the planar cobalt(II)-complex may be the steric conditions favorable for the square-planar co-ordination of the metal-ion. Thus, if bis(salicylaldoximato)cobalt(II) is assumed to be a planar trans-complex, a strong hydrogen bond of an O—H—O type may be possible. This is probably one of the factors which favor the planar co-ordination of salicylaldoximato-complex of cobalt(II). In this connection, it is of significance that a strong hydrogen bond of an O—H—O type has been reported to exist in bis(salicylaldoximato)nickel(II).[13]

The crystals of bis(salicylaldiminato)cobalt(II) are readily oxidized in the air, and their solubility in solvents is generally low, so that the measurement of the spectrum was not very easy. With precautions to prevent oxidation, the qualitative absorption spectra of the compound in chloroform and in ethyl methyl ketone were determined; the results are given in Fig. 3 and Table I. The spectra in the two different solvents coincide essentially with each other in all important points.

Bis(salicylaldiminato)cobalt(II) in non-co-ordinating solvents has a quadri-co-oridinate, planar configuration; the spectrum of this compound, which shows a sharp peak at about 24.8×10^{13} sec^{-1}, is regarded as characteristic of the quadri-co-ordinate, planar cobalt(II)-complex.

As will be described in a forthcoming paper, bis(*N*-*n*-alkylsalicylideneiminato)cobalt(II) complexes, which are derived by substituting *n*-alkyl groups for the hydrogen atoms of bis(salicylaldiminato)cobalt(II), take a tetrahedral co-ordination around the cobalt(II) ion. This remarkable change in configuration, caused by a change of a substitutent, may be due partly to the fact that the ligand field produced by the salicylideneiminate group is stronger than that produced by the *N*-*n*-alkylsalicylideneiminate group. In addition to this there may be cited the possibility that hydrogen bonding of an N—H—O type would be formed in bis(salicylideneiminato)cobalt(II) when the complex is trans-planar.

In the light of the findings of the present

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[13] L. L. Merritt, C. Guare and A. E. Lessor, *Acta Cryst.*, **9**, 253 (1956).
[14] J. F. Fackler, *Inorg. Chem.*, **2**, 266 (1963).

work, the configuration of bis(acetylacetonato)-cobalt(II) may be discussed. The complex has a magnetic moment correspondig to three unparied electrons, and a planar configuration would be ruled out by the conventional argument of magnetism. The complexes of cobalt(II), whose configurations have been firmly established as planar, are all of a low-spin type, with a magnetic moment corresponding to one unpaired election. On the basis of theoretical consideration, however, Cotton and Holm(6) claimed that bis(acetylacetonato)cobalt-(II) was a rare example of a planar cobalt-(II)-complex of a high-spin type. Its electronic absorption spectra, its ligand field bands in particular, are quite different from the spectra of the typical planar cobalt(II)-complexes studied in the present work. Thus, the square-planar configuration of bis(acetylacetonato)-cobalt(II) is to be rejected; there is no warrant for assuming the existence of planar cobalt(II)-complexes of a high-spin type, none of which have ever been established with reasonable certainty. It has also been pointed out recently that the association of the cobalt-(II)-complexes occurs to some extent, a sexa-co-ordination around the cobalt(II)-ion being thereby completed(14).

Summary

In order to establish the electronic absorption spectra of quadri-co-ordinate, square-planar cobalt(II)-complexes, the absorption spectra of bis(salicylaldehyde)ethylenediiminato- and bis-(salicylaldehyde)propylenediiminato-cobalt(II) in solution have been determined, with the utmost care taken to avoid undesirable oxidation of the complexes. These compounds show characteristic ligand field band, with a comparatively sharp peak in the near-infrared region.

Bis(salicylaldehyde)-α-α'-dimethylethylenediiminato- and bis(salicylaldehyde)-α,α'-diphenylethylenediiminato-cobalt(II) have deen prepared, and their spectra examined. These also show characteristic ligand field bands, with a sharp peak in the near-infrared region.

Bis(salicylaldoximato)- and bis(salicylaldiminato)-cobalt(II) have been prepared, and their spectra examined. On the basis of the results obtained above, it has been concluded that these two complexes take a quadri-co-ordinate, planar configuration.

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