The Preparation and the Co-ordination Chemistry of Cobalt Complexes with Schiff Bases Derived from Salicylaldehyde and Alkyl Amines

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The cobalt complexes of Schiff bases involve many problems of fundamental importance in the co-ordination chemistry of cobalt. As a step to the elucidation of these problems, the present authors previously characterized and discussed the electronic absorption spectra of the Schiff-base complexes of cobalt(II), which necessarily have a square-planar configuration because of their steric condition.1) It is now appropriate and possible to make a similar study of these cobalt complexes which are not necessarily required to take a square-planar configuration by the steric reason alone. The present paper deals with the preparation and the stereochemistry of cobalt(II) and cobalt(III) complexes of *N*-alkyl-salicylideneimines (Fig. 1).

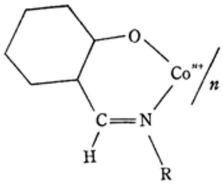

Fig. 1. Cobalt-complexes of *N*-alkyl-salicylideneiminate.

Experimental

Materials. — Bis(*N*-α-branched alkyl-salicylideneiminato) (cobalt(II) complexes were prepared in the atmosphere by the following two methods. 1)2) A mixture of calculated amounts of cobalt(II) acetate tetrahydrate, salicylaldehyde, and an α-branched-alkyl amine was heated in ethanol. To this solution a 4 N solution of sodium carbonate (about 75% of the calculated amount) was added to neutralize the acetic acid which was expected to be liberated

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

2) H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962).

in the reaction. When the solution was cooled or evaporated, the red crystals of the compound were obtained in a good yield. 2) Bis(salicylaldehyde)-cobalt(II) dihydrate, $Co(sal)_2 \cdot 2H_2O$,* and a slight excess of an α-branched alkyl amine were heated in methanol or ethanol for about ten minutes. When the solution was evaporated, red crystals were obtained in a good yield.

Bis(*N*-isopropyl- and bis(*N*-*s*-butyl-salicylideneiminato)cobalt(II) were reported previously.[2)]

Bis(*N*-*t*-butyl-salicylideneiminato)cobalt(II) was obtained in the form of prismatic red crystals. Recrystallization was carried out from ethanol. The crystals are quite soluble in common organic solvents.

Found: C, 64.41; H, 7.03; N, 6.73. Calcd. for $C_{22}H_{28}N_2O_2Co$: C, 64.2; H, 6.86; N, 6.81%.

The compound has also been reported by Sacconi et al.[3)]

Bis(*N*-1-ethylpropyl-salicylideneiminato)cobalt(II) was obtained in red, needle-like crystals. Recrystallization was carried out from *n*-hexane. It is very soluble in common organic solvents.

Found: C, 65.4; H, 7.41; N, 6.46. Calcd. for $C_{24}H_{32}N_2O_2Co$: C, 65.6; H, 7.34; N, 6.37%.

In general, the above-described compounds of cobalt(II) are stable, and they are not oxidized either in solution or in the crystalline state in the atmosphere.

Tris(*N*-*n*-alkyl-salicylideneiminato)cobalt(III) complexes were prepared by a method previously reported.[2)] There was a mistake in the original direction; a 4 N sodium carbonate ought to be employed instead of a 0.3 N solution.

All these cobalt(III) complexes, which are obtained as dark-green crystals, are very stable to the air both in the crystalline state and in solution.

Tris(*N*-methyl-,[4)] tris(*N*-ethyl-,[5)] tris(*N*-*n*-propyl-[2)] and tris(*N*-*n*-butyl-salicylideneiminato)cobalt(III)[2)] were reported earlier.

Bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II) complexes are readily oxidized by the atmospheric oxygen. For the preparation of these complexes, it is necessary to carry out the procedures in an oxygen free atmosphere. Recently Sacconi et al.[6)] reported the preparation of bis(*N*-*n*-butyl- and bis(*N*-*n*-amyl-salicylideneiminato)cobalt(II). The present authors have succeeded in preparing these complexes by the following novel method, which is also applicable to the synthesis of bis(*N*-*n*-alkyl-salicylideneiminato)-cobalt(II) in general: A methanolic solution of bis(salicylaldehyde)cobalt(II) dihydrate, $Co(sal)_2 \cdot 2H_2O$, and a trace of formaldehyde was boiled in a flask. When the space in the flask was filled with the methanol vapor, a slight excess of the amine was added quickly; then the flask was closed with a stopper in order to prevent the air from coming in. The closed flask was heated under stirring at the boiling temperature of the solvent for a reaction period of from 10 to 40 min.; then the solution was left to cool. The crystals which separated out were filtered quickly in the air and dried in vacuo.

For the preparation of bis(*N*-methyl-salicylideneiminato)cobalt(II), 3.0 g. of bis(salicylaldehyde)-cobalt(II) dihydrate and 2.5 ml. of a 30% aqueous solution of methyl amine were used, with 60 ml. of methanol, as a solvent, containing 2 ml. of a 37% formaldehyde solution. Following the general method described above, the reaction was continued for 10 min. at about 60°C. After the closed flask was left at room temperature for a day, brown crystals separated out.

Found: C, 58.7; H, 4.98; N, 8.58. Calcd. for $C_{16}H_{16}N_2O_2Co$: C, 58.7; H, 4.92; N, 8.56%.

Bis(*N*-ethyl-salicylideneiminato)cobalt(II) was prepared from 3.0 g. of bis(salicylaldehyde)cobalt(II) dihydrate and 1.4 g. of a 70% aqueous solution of ethyl amine. The solvent used was methanol (60 ml.) containing 26 ml. of water and 2 ml. of a 37% aqueous solution of formaldehyde. The general method was followed, the reaction being continued for 30 min. at 60°C. After the reaction was over, the cooled flask was left at room temperature for a day; well developed red plate-like crystals then separated out.

Found: C, 60.9; H, 5.67; N, 7.80. Calcd. for $C_{18}H_{20}N_2O_2Co$: C, 60.9; H, 5.67; N, 7.89%.

Bis(*N*-*n*-propyl-salicylideneiminato)cobalt(II) was prepared and red crystals by a method similar to that used in the case of bis(*N*-ethyl-salicylideneiminato)cobalt(II).

Found: C, 62.9; H, 6.41; N, 7.08. Calcd. for $C_{20}H_{24}N_2O_2Co$: C, 62.7; H, 6.31; N, 7.31%.

Bis(*N*-*n*-butyl-salicylideneiminato)cobalt(II) was prepared in red crystals from 3.0 g. of bis(salicylaldehyde)cobalt(II) dihydrate and 2.5 g. of *n*-butyl amine. The solvent employed was methanol (80 ml.) containing 2 ml. of a 37% aqueous solution of formaldehyde. The same general method was followed, the reaction being continued for about 10 min. at 60°C.

Found: C, 64.3; H, 6.78; N, 6.83. Calcd. for $C_{22}H_{28}N_2O_2Co$: C, 64.2; H, 6.85; N, 6.81%.

This complex has also been prepared by Sacconi et al.[6)] by a more complicated method.

Bis(*N*-benzyl-salicylideneiminato)cobalt(II) was prepared from 3.5 g. of bis(salicylaldehyde)cobalt-(II) dihydrate and 3.5 g. of benzyl amine, with 60 ml. of methanol as a solvent. The same general method was followed, the reaction being continued for about 20 min. at 60°C. After the flask, in which crystals of the compound had already started to separate out, was left to cool, well-developed red crystals were collected. This compound had been prepared previously by Endo[4)] using another method.

Found: C, 70.0; H, 5.02; N, 5.77. Calcd. for $C_{28}H_{24}N_2O_2Co$: C, 70.2; H, 5.05; N, 5.84%.

Comparison shows that this compound, which gradually undergoes oxidation in organic solvents in the atmosphere, is less stable to oxidation than the *N*-α-branched alkyl-derivatives, but more stable than the corresponding *N*-*n*-alkyl-derivatives.

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* The notation "sal" represents an anion formed when a proton is liberated from a molecule of salicylaldehyde.

3) L. Sacconi, P. Paoletti and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963).

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

5) B. O. West, *J. Chem. Soc.*, **1952**, 3115.

6) L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

Measurements.—The electronic absorption spectra of the complexes in solution were determined with a Beckman DU spectrophotometer. The solvents used were chloroform, benzene, ethanol and pyridine. It was confirmed that Beer's law was obeyed in the concentration range of the present work, which varied between 10^{-2} and 10^{-5} molar.

Results and Discussion

Cobalt(II) Complexes of Schiff Bases Derived from Salicylaldehyde and α-Branched Alkyl Amines.—Examination with a Stewart model shows that the steric condition due to the *t*-butyl groups prevents bis(*N*-*t*-butylsalicylideneiminato)cobalt(II) from taking a planar configuration.⁷⁾ The absorption spectrum of this compound in benzene, which is shown in Fig. 2, is essentially similar to the spectrum of the compound in such other organic solvents as methanol, ethanol and pyridine; therefore, no remarkable solvent effect on the structure of the molecules is present in the case of this compound. The absorption bands due mainly to the ligand groups come into the region of quite low frequencies, being superposed on a part of the ligand-field bands. It is generally possible, however, to see the main features of the ligand-field bands of these cobalt complexes. The ligand-field bands are quite different from those of the related cobalt(II) complexes with a square-planar configuration.¹⁾ The spectum of bis(*N*-*t*-butylsalicylideneiminato)cobalt(II) also bears an apparent resemblance to the spectrum of such tetrahedral cobalt(II) complexes as tetrahalogeno-cobalt(II) ions. As with the spectra of tetrahalogeno-cobalt(II) complexes with a tetrahedral configuration, the absorption band of bis(*N*-*t*-butylsalicylideneiminato)cobalt(II) with the main peak at about 24.6×10^{13} sec^{-1} is assigned to the spin-allowed transition, $^4A_2\rightarrow{}^4T_1(F)$. The next band, at 54 to 60×10^{13} sec^{-1}, is similarly assigned to the transition $^4A_2\rightarrow{}^4T_1(P)$. In the corresponding *s*-butyl, isopropyl or 1-ethylpropyl complexes, the steric hindrance to the square-planar configuration is more or less serious enough to prevent the square-planar configuration, but this is not so complete as in the case of the *t*-butyl derivative. The absorption spectra of these complexes in non-donor solvents, however, are quite similar to the spectrum of the *t*-butyl-complex with ligand-field bands in the visible and near-infrared regions characteristic of the tetrahedral cobalt(II) complexes (Fig. 2). It may be concluded that bis(*N*-isopropyl-, bis(*N*-*s*-butyl- and bis(*N*-1-ethylpropyl-salicylideneiminato)cobalt(II) are distorted significantly from the square-planar configuration. The assignment of the ligand-field bands of these tetrahedral complexes is made in a way similar to that used for the *t*-butyl complex.

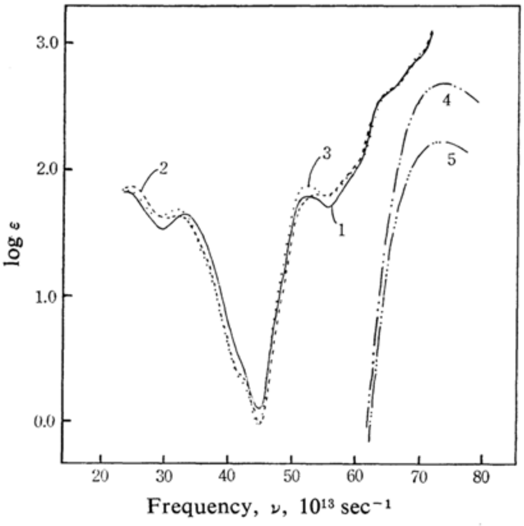

Fig. 2. Electronic absorption spectra of $Co(O\cdot C_6H_4\cdot CH:NR)_2$ in benzene and $HO\cdot C_6H_4\cdot CH:NR'$ in chloroform.
1, R=Isopropyl (——)
2, R=*t*-Butyl (----)
3, R=1-Ethylpropyl (······)
4, R′=*t*-Butyl (—··—)
5, R′=isopropyl (—···—)

It is significant that bis(*N*-α-branched alkyl-salicylideneiminato)cobalt(II) complexes show quite similar spectra, with absorption bands at nearly identical frequencies, when the substituent represents *t*-butyl, isopropyl, *s*-butyl, 1-ethylpropyl and cyclohexyl groups. Since the extent of the steric hindrance to the square-planar configuration of the cobalt(II)-complex is expected to be different for these substituents, the above observation suggests that the distortion from the square-planar configuration occurs to a nearly equal extent among all the above cobalt(II) complexes with α-branched alkyls as substituents. Judging from the considerable distortion from the square-plane in the case of the *t*-butyl-derivative, it is concluded that the tetrahedral configuration is most likely for these cobalt(II) complexes.

Cobalt-Complexes of Schiff Bases Derived from Salicylaldehyde and *n*-Alkyl Amines.—In the preceding part of this paper, it has been concluded that the configuration around the cobalt(II) ion in bis(*N*-α-branched alkyl-salicylideneiminato)cobalt(II) complexes is tetrahedral. It seemed interesting, therefore, to examine whether the configuration around the cobalt(II) ion is tetrahedral or square-planar in bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II)

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

complexes, in which there is no serious steric hindrance to either the tetrahedral or the square-planar configuration.

The *N*-*n*-alkyl-substituted complexes of cobalt(II) are so readily oxidized that these complexes can not be prepared by the conventional procedures in the atmosphere which have proved applicable to the preparation of the *N*-α-branched alkyl-complexes. Diehl and Chao[8] reported the preparation of bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II) with methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl groups as the substituent. These compounds, however, were not obtained in the form of crystals, but only as a solid mass. Sacconi et al.[6] recently reported the *n*-butyl- and *n*-amyl-derivatives of this series, but their method is not quite suitable for the preparation of the methyl-, ethyl- and *n*-propyl-derivatives, which are particularly susceptible to oxidation.

The present authors succeeded in synthesizing cobalt(II) complexes of the Schiff bases, with methyl, ethyl, *n*-propyl and *n*-butyl as the substituent, by means of a new method which proved applicable to the synthesis of the corresponding compounds with higher alkyls. The electronic spectra may be used diagnostically in examining the configuration of the cobalt(II) complexes of this type, since the spectrum of the square-planar cobalt(II) complex is quite different from that of the tetrahedral cobalt(II) complex.[1,2,7] Bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II) complexes all show absorption spectra similar to each other and to the spectra of bis(*N*-α-branched alkyl-salicylideneiminato)cobalt(II) complexes (cf. Fig. 3). It may be concluded that these bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II) complexes have a tetrahedral configuration.[9] In the spectra of bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II), an absorption band with the main peak at about $25\times10^{13}\,\mathrm{sec}^{-1}$ is assigned to a transition ${}^4A_2\rightarrow{}^4T_1(F)$.

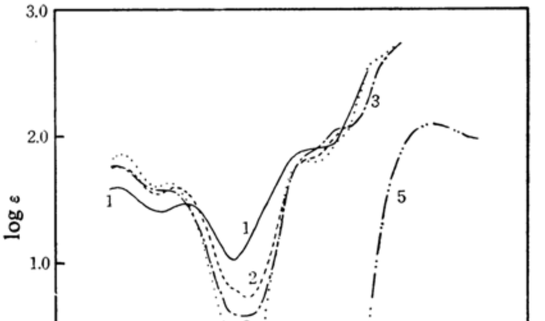

Fig. 3. Electronic absorption spectra of Co$\cdot$($O\cdot C_6H_4\cdot CH:NR)_2$ and $HO\cdot C_6H_4\cdot CH:NR'\cdot$
1, R=Methyl, in methylene dichloride (——)
2, R=Ethyl, in ethanol (----)
3, R=Benzyl, in ethanol (—·—)
4, R=*t*-Butyl, in benzene (······)
5, R′=Methyl, in chloroform (—··—)

The absorption maxima of the ligand-field bands of the *n*-alkyl-substituted cobalt(II) complexes are nearly identical with those of the *t*-butyl-derivative, which is regarded as remarkably distorted from the square-planar configuration on the steric ground alone. In the corresponding complexes of copper(II) and nickel(II), a gradual shift of the ligand-field band toward a lower frequency was observed in the following order, depending upon the extent of the distortion from the square-plane: *n*-alkyl, isopropyl, *t*-butyl.[7] It may, therefore, be concluded that the distortion from the square-planar configuration in bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II) complexes is as great as in the corresponding *t*-butyl derivative. It is thus clear that the configuration of the bis(*N*-alkyl-salicylideneiminato)cobalt(II) complexes, in general, is tetrahedral, whether or not there is steric hindrance to the square-planar configuration. The configuration around the cobalt(II) ion in bis(*N*-*n*-butyl-salicylidene iminato)cobalt(II) has been reported to be tetrahedral from magnetic measurements and X-ray powder photographs.[6,10]

Comparison readily reveals that the tetrahedral configuration is much more stabilized in the cobalt(II) complex than in the nickel(II) and the copper(II) complex[7] when complexes with identical ligands are compared. This is in agreement with what has been predicted on the basis of the crystal-field theory,[11] which demands much more crystal-field stabilization energy for the cobalt(II) ion with a d^7 configuration than for the nickel(II) and copper(II) ions. The color of bis(*N*-methyl-salicylideneiminato)cobalt(II) in the solid state is different from that of the other bis(*N*-alkyl-salicylideneiminato)cobalt(II) in the solid state,

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

[9] It was formerly stated that bis(*N*-methyl-salicylideneiminato)cobalt(II) was square-planar (H. Nishikawa, S. Yamada and R. Tsuchida, *Z. anorg. u. allg. Chem.*, **316**, 278 (1962)). In the light of the present work, this statement is not correct, although the configuration of the corresponding cobalt(II) complexes of ethyl, propyl and higher alkyls was correctly concluded in that paper to be distorted from the square-planar configuration.

[10] E. Frasson and C. Panatoni, *Z. Krist.*, **116**, 154 (1961).

[11] See, for example, L. E. Orgel, "An Introduction to Transition-metal Chemistry," Methuen and Co., London (1961).

although both of them consist of tetrahedral molecules in non-donor solvents. The examination of the methyl-substituted complex in the solid state is now in progress; it will be reported later, together with other materials.

The electronic absorption spectra of bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II) complexes in pyridine have been examined; some of them are shown in Fig. 4. The spectra of these *n*-alkyl-derivatives in pyridine, which are quite different from the spectra of the same compounds in non-donor solvents, may be interpreted as those of the sexa-co-ordinate cobalt(II) complexes. It may, therefore, be concluded that bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II) complexes in pyridine combine with two additional pyridine molecules to form sexa-co-ordinate complexes of cobalt(II). In agreement with this seems to be a fact that the recrystallization from pyridine of these cobalt(II) complexes yields crystals of the compounds with two molecules of pyridine per formula, molecules which are most probably bound with the cobalt(II) ion.

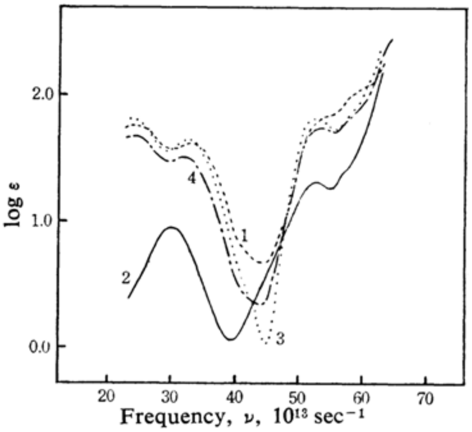

Fig. 4. Electronic absorption spectra of Co·$(O\cdot C_6H_4\cdot CH:NR)_2$.
1, R=*n*-Butyl, in ethanol (----)
2, R=*n*-Butyl, in pyridine (——)
3, R=*s*-Butyl, in ethanol (······)
4, R=*s*-Butyl, in pyridine (—·—)

The absorption band at about 30×10^{13} sec^{-1} is assigned to the $^4T_{1g}\rightarrow{}^4T_{2g}$ transition, and the absorption band at about 53.6×10^{13} sec^{-1}, to the $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ transition, on the basis of the notation of the O_h field symmetry.

On the contrary, the *N*-α-branched alkyl complexes keep their tetrahedral configuration in pyridine, since their spectra in pyridine are closely similar to their spectra in non-donor solvents (Fig. 4) and since they give no pyridine adducts on recrystallization from pyridine. This behavior is considered to be due partly to the steric condition originating from the branched alkyl groups, which prevent a pyridine molecule from combining with the cobalt(II) ion to a greater or lesser extent. This behavior also shows that the tetrahedral configuration is more favored for cobalt(II) than for nickel(II), since bis(*N*-isopropyl-salicylideneiminato)nickel(II) in pyridine, for example, is sexa-co-ordinate with the solvent molecules combined.[12] It is worth noting that this is exactly the case with the cyclohexyl-derivative. Bis(*N*-cyclohexyl-salicylideneiminato)cobalt(II) in pyridine does not keep a tetrahedral configuration, but probably forms a quinque-co-ordinate complex of cobalt(II), with a molecule of pyridine as one of the ligands.[13]

Tris(*N*-*n*-alkyl-salicylideneiminato)cobalt(III).—The electronic spectra of tris(*N*-*n*-alkyl-salicylideneiminato)cobalt(III) complexes, which are very stable in the atmosphere, are quite similar to each other. Only some of them are, therefore, shown in Fig. 5. The spectra

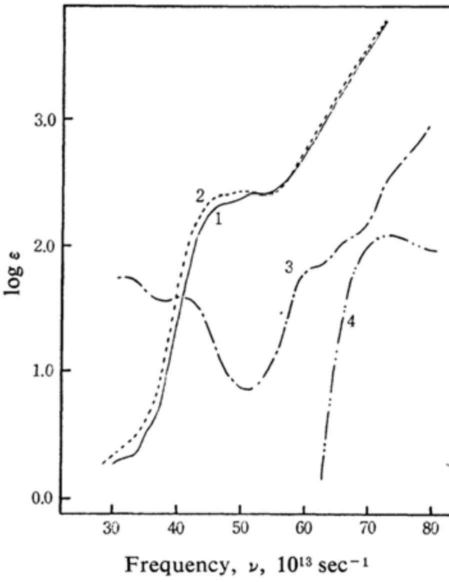

Fig. 5. Electronic absorption spectra of:
1, $Co(O\cdot C_6H_4\cdot CH:N\cdot CH_3)_3$, in benzene (——);
2, $Co(O\cdot C_6H_4\cdot CH:N\cdot n\text{-}C_3H_7)_3$, in benzene (----);
3, $Co(O\cdot C_6H_4\cdot CH:N\cdot n\text{-}C_3H_7)_2$, in ethanol (—·—);
4, $HO\cdot C_6H_4\cdot CH:N\cdot CH_3$, in chloroform (—··—).

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[12] S. Yamada and H. Nishikawa, unpublished.

[13] The pyridine solution of the cyclohexyl-substituted complex obeys Beer's law; therefore, an equilibrium between the original complex and the pyridine adduct seems to be non-existent. Upon recrystallization from pyridine, this cobalt(II)-complex yields an adduct with one molecule of pyridine. The details will be presented later elsewhere.

of these complexes, which are quite different from the spectra of the cobalt(II)-complexes with the corresponding Schiff bases show, a ligand-field band at about $50\times10^{13}\,\mathrm{sec}^{-1}$, a band which is assigned to the ${}^1A_{1g}\rightarrow{}^1T_{1g}$ transition in the notation of the O_h field symmetry. Judging from the maximum frequency of this band, the Schiff bases of this type stand a little higher than water and acetylacetonate, but much lower than ammonia in the spectrochemical series.

Bis(*N*-α-branched alkyl-salicylideneiminato)-cobalt(II) is stable in solution as well as in the solid state. An ordinary procedure of refluxing cobalt(II) acetate, salicylaldehyde and one of the α-branched alkyl amines in the atmosphere yields the cobalt(II)-complex, but no cobalt(III)-complex. So far, all attempts with α-branched alkyls as a substituent, even those using oxidizing agents, to prepare tris-(*N*-alkyl-salicylideneiminato)cobalt(II) have been unsuccessful. This is probably due to the steric condition. This also shows the relatively high stability of the tetrahedral configuration for bis(*N*-α-branched alkyl-salicylideneiminato)cobalt(II).

The Relative Stability of Tetrahedral Cobalt-(II) Complexes.—The tetrahedral bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II) complexes are much more easily oxidized to give tris(*N*-*n*-alkyl-salicylideneiminato)cobalt(III) than the corresponding *N*-aryl-substituted cobalt(II)-complexes. Thus, by refluxing cobalt acetate, salicylaldehyde and one of the *n*-alkyl amines in the atmosphere, the cobalt(III) complexes of the Schiff bases are obtained in the form of dark green crystals, while a similar procedure using aromatic amines instead of the *n*-alkyl amines yields red crystals of the cobalt-(II) complexes of the corresponding Schiff bases. Moreover, when heated on a water-bath, tris-(*N*-aryl-salicylideneiminato)cobalt(III)-complexes in solution convert themselves into the cobalt(II)-complexes, while tris(*N*-*n*-alkyl-salicylideneiminato)cobalt(III)-complexes do not.

This difference between *n*-alkyl and aromatic amines may be due partly to the steric factor, which destabilizes the octahedral tris(*N*-aryl-salicylideneiminato)cobalt(III)-complexes. This fact also seems to show that the *N*-*n*-alkyl-salicylideneiminate yields a stronger ligand field than the *N*-aryl-salicylideneiminate ion, since it is known that the higher stability of the sexa-co-ordinate cobalt(III)-complex is attained with ligands producing a stronger ligand field.

The stability of the quadri-co-ordinate cobalt-(II)-complex to oxidation by atmospheric oxygen seems to be correlated with the strength of the field produced by the ligands. Inspection shows that, in the spectrochemical series, water as ligand lies on the border above which the cobalt(III)-complex is more stable than the cobalt(II)-complex in the atmosphere. Thus the hexaquo-cobalt(III)-complex is known although it readily changes into the hexaquo-cobalt(II)-complex. On the other hand, the acetylacetonate ion, which is just above water in the series, forms a stable cobalt(III)-complex, but its cobalt(II)-complex is readily oxidized to yield the cobalt(III)-complex in the atmosphere, unless sexa-co-ordinate diaquo-bis(acetylacetonato)cobalt(II) is formed. Since *N*-alkyl- or *N*-aryl-salicylideneiminate ions lie slightly above water and acetylacetonate in the spectrochemical series, the observed stability of *N*-substituted salicylideneiminato-cobalt-complexes is found to be understandable in terms of the strength of the ligand field. Inspection also reveals that those ligands, such as halide and isothiocyanate, which stand below acetylacetonate in the spectrochemical series form tetrahedral cobalt(II)-complexes which are stable in the atmosphere, unless sexa-co-ordinate complexes are formed.

Bis(*N*-benzyl-salicylideneiminato)cobalt(II).—Bis(*N*-benzyl-salicylideneiminato)cobalt(II) in non-donor solvents shows an absorption spectrum quite similar to the spectra of the other cobalt(II)-complexes which have been concluded to be tetrahedral (Fig. 3). It may similarly be concluded that the *N*-benzyl-substituted complex of cobalt(II) has a tetrahedral co-ordination.

The compound is comparatively stable to oxidation in the atmosphere. The stability of the complex to oxidation seems to lie between that of the *N*-*n*-alkyl and *N*-α-branched alkyl derivatives, as may be inferred from the following properties of these complexes: 1) The *N*-benzyl-substituted cobalt(II) is considerably stable in the atmosphere, while the *N*-*n*-alkyl-derivatives of cobalt(II) are very susceptible to the atmospheric oxygen and are likely to give the cobalt(III)-complexes. When left in the air for a long time, however, the *N*-benzyl-derivative of cobalt(II) undergoes oxidation to the cobalt(III) state. 2) In the typical procedure using cobalt(II) acetate, salicylaldehyde and benzyl amine in the atmosphere, bis(*N*-benzyl-salicylideneiminato)cobalt-(II) is formed as red crystals; on prolonged heating these crystals are changed into dark green crystals of tris(*N*-benzyl-salicylideneiminato)cobalt(III).

This behavior may be regarded as showing that the field of *N*-benzyl-salicylideneiminate to the metal ion is weaker than that of the *N*-alkyl-substituted one but stronger than that of the *N*-aryl-substituted one.

Summary

A novel method has been described for preparing bis(*N*-*n*-alkyl-salicylideneiminato)cobalt(II), where *n*-alkyl represents methyl, ethyl, *n*-propyl, *n*-butyl and higher alkyls. Bis(*N*-α-branched alkyl-salicylideneiminato)cobalt(II)-complexes have been prepared by a simpler method, where α-branched alkyl denotes isopropyl, 1-ethylpropyl, *s*-butyl, *t*-butyl and cyclohexyl. The benzyl derivative has also been prepared. Tris(*N*-*n*-alkyl-salicylideneiminato)cobalt(III) complexes have been prepared.

On the basis of electronic absorption spectra, it has been concluded that bis(*N*-alkyl-salicylideneiminato)cobalt(II)-complexes have a tetrahedral configuration, whether the alkyl used as a substituent represents an *n*-alkyl or an α-branched alkyl.

The relative stability and the configuration of cobalt(II)-complexes have been discussed.

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