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Cobalt(II) Complexes of Schiff Bases Derived from 3-Methoxysalicylaldehyde and Amines

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Bis(*N*-substituted-3-methoxysalicylideneiminato)cobalt(II) complexes, including several new compounds, have been prepared, and their configurations examined. It has been concluded that these cobalt(II) compounds take a tetrahedral configuration of a high-spin type in non-donor solvents and in the solid state. For R=*n*-alkyl and monosubstituted phenyl, these complexes in pyridine take an octahedral configuration, with two pyridine molecules bound to the cobalt(II) ion. However, bis(*N*-2′, 6′-dimethylphenyl- and bis(*N*-2′, 6′-diethylphenyl-3-methoxysalicylideneiminato) complexes take a hexa-coordinate, though considerably distorted, configuration in pyridine. This behaviour is different from that of the corresponding salicylideneiminato-complexes of cobalt(II). The results of the present work are compared with the findings on the corresponding salicylideneiminato-complexes.

The preparation and the configurations of cobalt complexes of Schiff bases derived from salicylaldehyde and amines have been described in previous papers.[1-3] As an extension of these studies, the cobalt(II) complexes of *N*-substituted 3-methoxysalicylideneimines*[1] (Fig. 1) have been synthesized and their structures have been studied in the present work. It is also one of the purposes of the present work to examine the effect of the substituent, the 3-methoxy radical, on the configuration of the cobalt(II) complexes, and to compare the cobalt(II) complexes of the 3-methoxysalicylideneimines with those of the salicylideneimines.

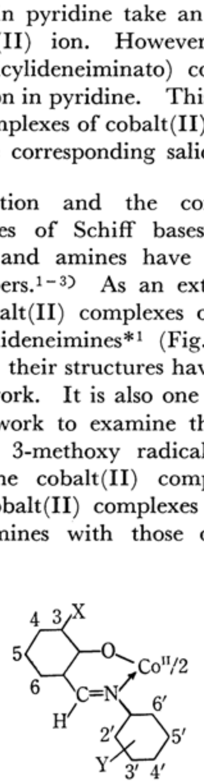

Fig. 1. Schiff base cobalt(II) complex.

Experimental

Materials. Cobalt(II) complexes of Schiff bases derived from 3-methoxysalicylaldehyde and amines were prepared by the following general method. To a solution of cobalt(II) acetate tetrahydrate (0.01 mol) in methanol (20 m*l*), a solution of 3-methoxysalicylideneimine (0.02 mol) in methanol (20 m*l*) was added. The reaction mixture was then stirred continuously at 50—55°C for about one hour, and potassium ethanolate (0.02 g atom of potassium in 20 m*l* of ethanol) was gradually added to the solution. Concentration by distillation under reduced pressure yielded orangered crystals of the Schiff base cobalt(II) complex. Purification of the complexes were made by recrystallization from methanol, ethanol, or chloroform. They are stable to oxidation in the atmosphere at room temperature. Elemental analyses of the new compounds prepared in this work are given in Table 1.

TABLE 1. ELEMENTAL ANALYSES OF BIS(*N*-SUBSTITUTED PHENYL-3-METHOXYSALICYLIDENEIMINATO)-COBALT(II), $Co(3\text{-}CH_3O\cdot Sal\cdot R)_2$

R	Calcd., %			Found, %		
	C	H	N	C	H	N
n-C_3H_7	59.06	7.26	6.26	59.15	6.38	6.65
n-C_4H_9	61.14	6.84	5.94	60.74	6.87	6.06
iso-C_3H_7	59.06	7.21	6.26	59.10	6.96	6.41
t-C_4H_9	61.14	6.84	5.94	61.22	6.75	6.12
Cyclohexyl	64.24	6.94	5.35	64.16	6.92	5.44
Ph	65.76	4.73	5.48	65.74	4.73	5.47
4′-CH_3Ph	66.79	5.23	5.19	66.87	5.47	5.12
2′, 6′-$(CH_3)_2$Ph	67.72	5.68	4.93	67.82	5.72	4.84
2′, 6′-$(C_2H_5)_2$Ph	68.10	6.72	4.67	68.21	6.50	4.34

The bis(*N*-substituted-salicylideneiminato)cobalt(II) complexes used in this work had been reported previously,[1] except for bis(*N*-2′, 6′-diethylphenyl-salicylideneiminato)cobalt(II), which was prepared by a method similar to that employed previously.

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*[1] Abbreviated as $Co(3\text{-}CH_3O\cdot Sal\cdot R)_2$ in the present paper.

1) a) H. Nishikawa and S. Yamada, This Bulletin, **37**, 8 (1964); b) *ibid.*, **37**, 1154 (1964); c) *ibid.*, **38**, 1506 (1965).

2) H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962); *Z. anorg. u. allgem. Chem.*, **316**, 278 (1962).

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

Found: C, 72.43; H, 6.49; N, 5.02%. Calcd for $C_{34}H_{36}N_2O_2Co$: C, 72.46; H, 6.44; N, 4.97%.

Measurements. The electronic absorption spectra of the compounds in solution were determined with a Shimadzu QR-50 spectrophotometer in the near-infrared, visible, and ultraviolet regions at room temperature. Pyridine for a solvent was purified, whenever necessary, by distillation after having been dried over barium oxide. The reflectance spectra of the compounds in the solid state were determined with a Shimadzu QR-50 spectrophotometer.

The magnetic measurements were carried out by Gouy's method at room temperature.

Results and Discussion

The previous studies[1,4,5] revealed that it was possible to synthesize numerous cobalt(II) complexes of the Co(Sal·2′-XPh)$_2$*2 and the Co(Sal·2′, 6′-Y$_2$Ph)$_2$ types, which had previously been believed to be non-existent. The present work also indicates that the cobalt(II) complexes of the Co(3-CH_3O·Sal·2′, 6′-Y$_2$Ph)$_2$ type can be prepared as orange-red crystals by a method similar to that employed previously,[1c] where Y denotes CH_3 or C_2H_5.

The electronic absorption spectrum of the cobalt(II) complex depends upon the configuration of the complex, and may be used diagnostically in discussing the configurations of the cobalt(II) complexes.[1-3] The examination of the electronic spectra (Fig. 2) indicates that the cobalt(II) complexes of the Co(3-CH_3O·Sal·R)$_2$ type in the solid state or in non-donor solvents are all tetrahedral and of a high-spin type, whether R represents an alkyl or an aryl radical. These spectra are quite similar to those of the corresponding *N*-substituted salicylideneiminato-cobalt(II) complexes, which were previously concluded to be tetrahedral and of a high-spin type.[1] The absorption bands at about 8 and 10.5×10^3 cm^{-1} may be considered to arise from the $^4T_1\leftarrow{}^4A_2$ transition in the notation of T_d field symmetry.

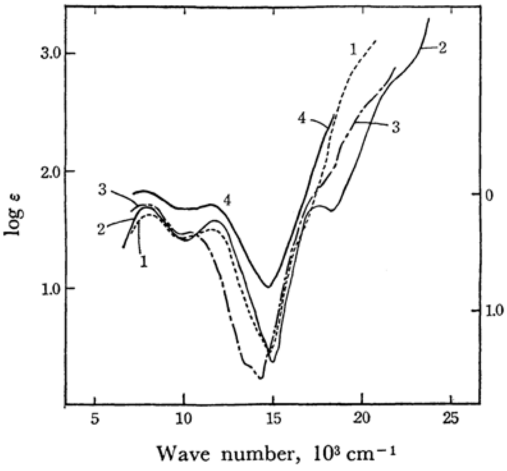

Fig. 2. Electronic spectra of Co(3-CH_3O·Sal·R)$_2$: 1, R=Ph in chloroform; 2, R=*n*-C_4H_9 in chloroform; 3, R=2′, 6′-(C_2H_5)$_2$Ph in benzene; 4, R=Ph in the solid state (by reflectance).

It is interesting to examine the stereochemistry of these cobalt(II) complexes in pyridine and to compare it with that of the complexes of the Co(Sal·R)$_2$ type.[1] When R represents an *n*-alkyl, a phenyl, and a 4′-methylphenyl, the electronic absorption spectra (Fig. 3) clearly show that these cobalt(II) complexes, which are tetrahedral in non-donor solvents, take an octahedral configuration in pyridine. The absorption bands at about 10.0 and 17.5×10^3 cm^{-1} may be assigned as $^4T_{2g}\leftarrow{}^4T_{1g}$ and $^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$ transitions respectively.

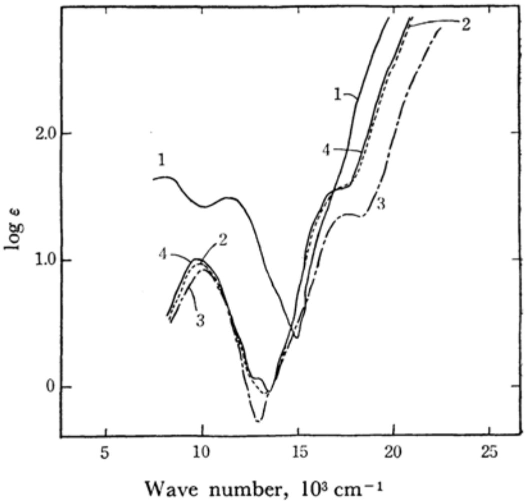

Fig. 3. Electronic spectra of Co(3-CH_3O·Sal·R)$_2$: 1, R=4′-CH_3Ph in chloroform; 2, R=4′-CH_3Ph in pyridine; 3, R=*n*-C_4H_9 in pyridine; 4, R=Ph in pyridine.

On the contrary, Co(3-CH_3O·Sal·*t*-C_4H_9)$_2$ retains the tetrahedral configuration in pyridine, since its electronic spectrum in pyridine is very similar to the spectrum characteristic of the tetrahedral cobalt(II) complexes (Fig. 4). This behavior of Co(3-CH_3O·Sal·*t*-C_4H_9)$_2$ in pyridine, which is similar to that of Co(Sal·*t*-C_4H_9)$_2$, is considered to be due to the steric condition originating from the bulky *t*-butyl groups. For R=*iso*-C_3H_7 or cyclohexyl, the steric hindrance is not as large as for R=*t*-C_4H_9, and it was previously concluded that in pyridine about 50% of the complex molecules were present in the tetrahedral form for Co(Sal·cyclohexyl)$_2$.[6] In a similar way, the

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[4] B. O. West, *J. Chem. Soc.*, **1962**, 1374.

[5] H. Nishikawa and S. Yamada, This Bulletin, **35**, 1430 (1962).

*2 The notations Ph and XPh denote a phenyl and a monosubstituted phenyl radical respectively.

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

present work shows that about 90% of the molecules exist as the tetrahedral species (the parent complex) for Co(Sal·*iso*-C_3H_7)$_2$, and that only about 15 and 20% of the molecules of the complex are in the tetrahedral form for Co(3-CH_3O·Sal·cyclohexyl)$_2$ and for Co(3-CH_3O·Sal·*iso*-C_3H_7)$_2$ repsectively when they are dissolved in pyridine.

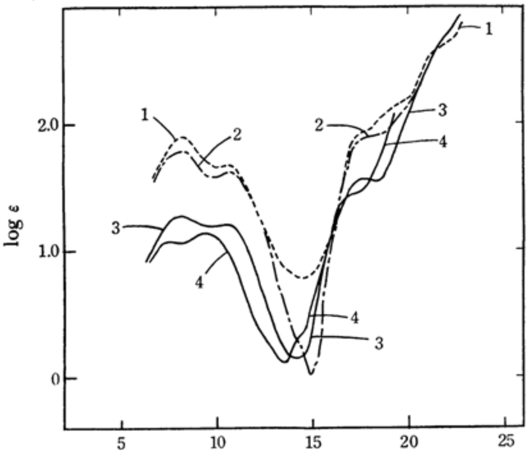

Fig. 4. Electronic spectra of Co(3-CH_3O·Sal·R)$_2$: 1, R=*t*-C_4H_9 in pyridine; 2, R=cyclohexyl in dichloromethane; 3, R=*iso*-C_3H_7 in pyridine; 4, R=cyclohexyl in pyridine.

When R represents 2′, 6′-$(CH_3)_2$Ph and 2′, 6′-$(C_2H_5)_2$Ph, the steric condition seems to make it difficult for two molecules of pyridine to be coordinated with the central cobalt(II) ion. In fact, it was concluded previously that Co(Sal·2′, 6′-$(CH_3)_2$Ph)$_2$ in pyridine existed predominantly as a penta-coordinate complex, with one pyridine molecule bound to the cobalt (II) ion, the tetrahedral species being also present as a minor component in equilibrium with the penta-coordinate pyridine solvate.7) The present work shows that the predominant species in the pyridine solution of Co(Sal·2′, 6′-$(C_2H_5)_2$Ph)$_2$ is a penta-coordinate complex, Co(Sal·2′, 6′-$(C_2H_5)_2$Ph)$_2$·Py,[*3] since the spectrum of the compound in pyridine is quite similar to the reflectance spectrum of Co(Sal·2′, 6′-$(CH_3)_2$Ph)$_2$·Py in the solid state, which was previously concluded to be penta-coordinate.7)

On the contrary, the electronic spectra of Co-(3-CH_3O·Sal·2′, 6′-Y_2Ph)$_2$ in pyridine, (Y_2 being $(CH_3)_2$ and $(C_2H_5)_2$), are quite different from the spectra of typical tetrahedral complexes of the Co(3-CH_3O·Sal·R)$_2$ type (Fig. 5) as well as from the spectra of the cobalt(II) complexes, which were previously concluded to be penta-coordinate.7,8)

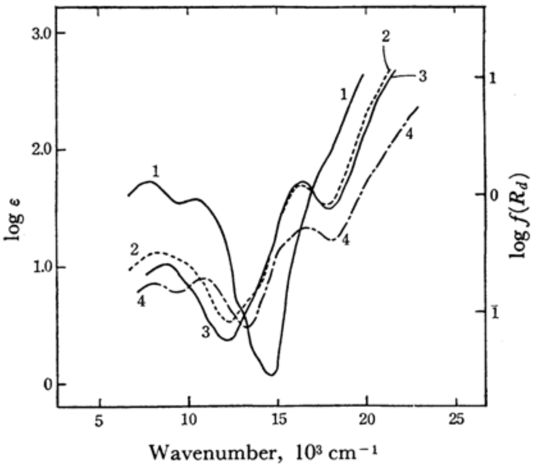

Fig. 5. Electronic spectra of Co(X·Sal·R)$_2$ and a pyridine solvate: 1, X=3-CH_3O, R=2′, 6′-$(CH_3)_2$Ph in chloroform; 2, X=3-CH_3O, R=2′, 6′-$(CH_3)_2$Ph in pyridine; 3, X=3-CH_3O, R=2′, 6′-$(C_2H_5)_2$Ph in pyridine; 4, Co(Sal·2′, 6′-$(CH_3)_2$-Ph)$_2$·Py in the solid state (by reflectance).

Since Beer's law is obeyed in the concentration range from 5×10^{-3} to 10^{-5} molar, no equilibrium consisting of two or more species seems to be present. The main features of the absorption spectrum of this cobalt(II) complex in pyridine may thus be interpreted on the basis of the model of the octahedral configuration. The predominant species in the pyridine solution is most probably the hexa-coordinate complex, Co(3-CH_3O·Sal·2′, 6′-Y_2Ph)$_2$(Py)$_2$. It is most likely, however, that the configuration is enormously distorted from the regular octahedron, since the band maximum (8.5×10^3 cm^{-1}) lies at a considerably lower frequency than the maximum of Co(3-CH_3O·Sal·4′-CH_3Ph)$_2$ in pyridine (10.0×10^3 cm^{-1}). Evidence for the existence of the hexa-coordinate complex may be afforded by the isolation and characterization of the possibly hexa-coordinate solvates, Co(3-CH_3O·Sal·2′, 6′-Y_2Ph)$_2$-(Py)$_2$9)

All the above findings seem to indicate that the tendency to attain six-coordination is higher for Co-CH_3O·2′, 6′-Y_2Ph)$_2$ than for Co(Sal·2′, 6′-Y_2Ph)$_2$, where Y denotes CH_3 or C_2H_5. It is evident that the difference in configuration of the pyridine solvate between the salicylideneiminato- and the 3-methoxy-salicylideneiminato-cobalt(II) complexes is due not to the steric factor, but, rather, to the difference in ligand-field strength between the two lignads. This conclusion is supported by the observation that bis(*N*-monomethylphenyl-acetylacetoneaminato)cobalt(II) complexes, in which the ligand field is stronger than in the

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[*3] The notation Py represents a pyridine molecule.

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

8) L. Sacconi, M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

9) S. Yamada and E. Yoshida, to be submitted soon elsewhere.

corresponding *N*-substituted salicylideneiminato complexes, retain the tetrahedral configuration even in pyridine.[10] It is interesting to note that only a slight chagne in the strength of the ligand field between salicylideneimine and the 3-methoxysalicylideneimine may produce such a remarkable difference in the configuration of the cobalt(II) complexes.[11]

The present authors are grateful to Miss Kuniko Yamanouchi for her experimental assistance, and to the Ministry of Education for financial support.

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[10] S. Yamada, E. Yoshida and Y. Kuge, Proceedings 9th Internat. Conf. Coordin. Chem. (9th ICCC) (ed. W. Schneider), Helv. Chim. Acta Verlag, Basel (1966), p. 68.

[11] S. Yamada, *Coordin. Chem. Review,* **1**, 415 (1966).