Schiff Base Cobalt(II) Complexes with Five-coordination

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It was previously concluded[1] that Co(sal.-2, 6-$(CH_3)_2$Ph)$_2$py[2] in the solid state consisted of the five-coordinate cobalt(II) complex of a high-spin type. We have recently examined a series of related compounds of the Co(X-sal.R)$_2$ type, and found several examples of the five-coordinate complexes with one pyridine molecule bound as the fifth ligand.

The complexes of the Co(X-sal.R)$_2$ type were prepared as orange-red cyrstals by a method similar to that employed for salicylideneiminato-complexes,[3] where X=5-Cl, 5-Br, 5-NO_2, 3, 5-Br_2 and 5, 6-benzo, and R=2, 6-$(CH_3)_2$Ph and 2, 6-$(C_2H_5)_2$Ph. Elemental analyses agreed with the above formula. Since the electronic spectra of cobalt(II) complexes depend upon the configuration of the complexes, the spectrum is regarded as diagnostic of the stereochemistry of the cobalt(II) complexes.[4] Spectral and magnetic examinations show that all the above complexes are tetrahedral and of a high spin type in non-donor solvents and in the solid state.

Their electronic absorption spectra in pyridine, however, are quite different from any of the spectra typical of the tetrahedral or of the octahedral cobalt(II) complexes. The spectra, some of which are shown in Fig. 1, bear a close resemblance to the spectra which were reported for the five-coordinate complexes of a high-spin type.[1,4,5] It is to be noted that Beer's law is obeyed for the pyridine solutions so that equilibrium is not possible, but only one species with five-coordination exists in the pyridine solutions. Thus it is concluded that the five-coordinate complexes of the Co(X-sal.R)$_2$py type are predominantly present in the pyridine solutions of the parent complexes prepared in the present work.

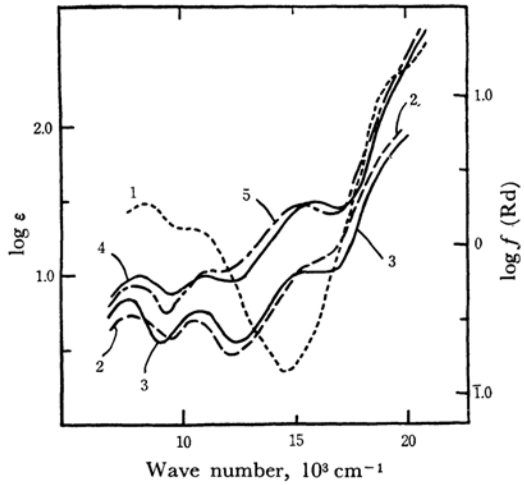

Fig. 1. Electronic absorption spectra of: 1, Co-(5, 6-benzo-sal.2, 6-$(CH_3)_2$Ph)$_2$ (by reflectance); 2, Co(5, 6-benzo-sal.2, 6-$(C_2H_5)_2$Ph)$_2$py (by reflectance); 3, Co(5, 6-benzo-sal.2, 6-$(CH_3)_2$Ph)$_2$py (by reflectance); 4, Co(5-Cl. sal. 2, 6-$(CH_3)_2$Ph)$_2$ in pyridine; 5, Co(5-Cl. sal. 2, 6-$(C_2H_5)_2$Ph)$_2$ in pyridine.

Some of these pyridine solvates were isolated as crystals. By adding a small amount of *n*-hexane to the hot solution of the parent complexes in pyridine, the pyridine solvates with the formula of Co(X-sal.R)$_2$py were isolated as brown crystals for the following pairs of X and R: (X=H, R=2, 4, 6-Br_3Ph), (X=5, 6-benzo, R=2, 6-$(CH_3)_2$Ph and (X=5, 6-benzo, R=2, 6-$(C_2H_5)_2$Ph). The elemental analyses agreed with the composition indicated above. These pyridine solvates, which have magnetic moments of 4.5—4.9 B. M. at room temperature, are concluded to be five-coördinate and of a high-spin type, from their electronic spectra, some of which are shown in Fig. 1.

The details will be reported elsewhere shortly.

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

[2] A cobalt(II) complex of a Schiff base derived from a substituted salicylaldehyde and amines of the type, RNH_2, is abbreviated as Co(X-sal.R)$_2$ in this communication. The notations, Ph and py, denote a phenyl group and a pyridine molecule, respectively.

[3] H. Nishikawa and S. Yamada, This Bulletin, **38**, 1506 (1965).

[4] H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962); S. Yamada, *Coordin. Chem. Rev.*, **1**, 415 (1966).

[5] M. Ciampolini, N. Nardi and G. P. Speroni, *ibid.*, **1**, 222 (1966).