Cobalt(II) Complexes with Schiff's Bases Derived from Salicylaldehyde and ortho-Substituted Aromatic Amines

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It has been generally believed that quadri-co-ordinate cobalt(II) complexes are not formed with Schiff's bases having substituents on the carbon atom in the 2-position (I)[1]. In fact, bis(salicylidene-2-anisilato)cobalt(II) was reported, but the formation of the compound was ascribed to extra stabilization due to the additional linkage of the oxygen atom of the methoxygroup with the cobalt(II) ion to complete sexa-co-ordination[1]. The present authors have recently succeeded in preparing several cobalt(II) compounds with Schiff's bases having substituents in the 2-position, which are listed in Table I.

The main procedure of the preparations was to add the mixture of $Co(salal)_2 \cdot 2H_2O$*1 (0.015 mol.) and one of the amines (about 0.045 mol.) into a flask which contained ethanol and was filled with its vapor above the liquid phase, keep the reaction mixture closed tightly, allow it to stand overnight and cool it eventually. Red or orange-red crystals are then obtained. In the case of the *o*-chloroaniline, dark-brown crystals are obtained by this procedure. These crystals were recrystallized from pyridine, and the resulting crystals of $Co(2\text{-}Cl \cdot C_6H_4 \cdot N : CH \cdot C_6H_4 \cdot O)_2 \cdot (py)_2$*2 were heated at 70°C in vacuo to yield orange-yellow crystals of $Co(2\text{-}Cl \cdot C_6H_4 \cdot N : CH \cdot C_6H_4 \cdot O)_2$.

Absorption spectra of these compounds in non-co-ordinating organic solvents have been determined in the present study. Since all these compounds display similar absorption spectra, only some of the typical spectra are shown in Fig. 1, together with the absorption spectra of bis(salicylidene-methyliminato)- and bis(salicylidene - isopropyliminato) - cobalt(II). Most bis(salicylidene-alkyliminato)cobalt(II) complexes, absorption spectra of which were recently reported by the present authors[2], are stable in the air at least during the measurements, except for the methyliminato compound of cobalt(II), which is unstable in the air. Since the measurements in the previous

1) B. O. West *Nature*, 173, 1187 (1954).

*1 The notation, salal, denotes an anion derived when a molecule of salicylaldehyde loses a hydrogen ion of the phenolic hydroxylgroup.

*2 The notation, py, denotes a molecule of pyridine.

2) H. Nishikawa, S. Yamada and R. Tsuchida, *Z. anorg. u. allgem. Chem.* (1962), in press.

TABLE I. BIS(SALICYLIDENE-ARYLIMINATO)COBALT(II), $Co(O\cdot C_6H_4\cdot CH:N\cdot R)_2$

R	Solvents used in preparation	C, %		H, %		N, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Methylphenyl	Ethanol	70.2	69.9	5.05	5.08	5.84	5.92
2-Chlorophenyl	Ethanol	60.0	60.3	3.49	3.61	5.38	5.22
2,6-Dimethylphenyl	Methanol	71.0	71.1	5.56	5.52	5.52	5.22
2,4-Dimethylphenyl	Ethanol	71.0	70.8	5.56	5.65	5.52	5.34
2,3-Dimethylphenyl	Methanol	71.0	70.7	5.56	5.53	5.52	5.86
α-Naphthyl	Methanol	74.0	73.6	4.39	4.36	5.08	4.96

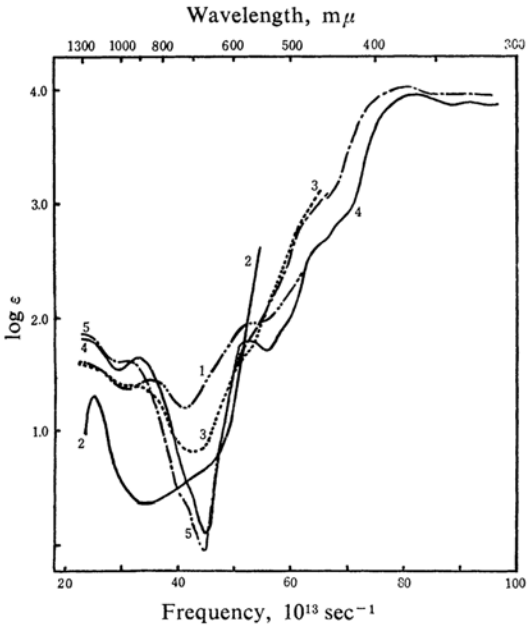


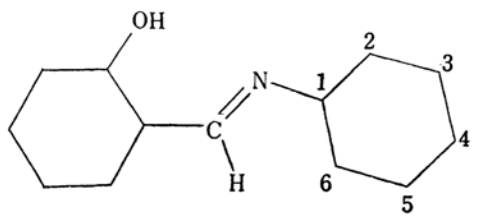
Fig. 1. Ultraviolet-absorption spectra of 1. $Co(O\cdot C_6H_4\cdot CH:N\cdot CH_3)_2$ in chloroform, 2. "salcomine" in chloroform, 3. $Co(O\cdot C_6H_4\cdot CH:N\cdot 2\text{-}Cl\cdot C_6H_4)_2$ in benzene, 4. $Co(O\cdot C_6H_4\cdot CH:N\cdot 2\text{-}CH_3\cdot C_6H_4)_2$ in benzene, and 5. $Co(O\cdot C_6H_4\cdot CH:N\cdot 2,6\text{-}(CH_3)_2C_6H_3)_2$ in benzene.

work[2] were done in the presence of air, it seems likely that the oxidation of the methyliminato compound may have taken place during the measurements. The measurements in the present work with bis(salicylaldehyde)ethylenediimine-cobalt(II), ("salcomine"), bis(salicylaldehyde)propylenediimine-cobalt(II) and bis(salicylidene-methyliminato)cobalt(II), which are most readily oxidized in the air, have been carried out in the atmosphere of nitrogen to avoid the undesirable oxidation.

It was formerly found that the absorption spectra, especially the ligand field bands, of the compounds of this sort are diagnostic in determining the configuration of these compounds[2]. Actually the present measurements indicate that "salcomine" and the corresponding propylenediimine complex, which have square-planar configuration, show absorption spectra quite different from the spectra of the methyliminato- and other alkyliminato-derivatives, which were concluded to have a configuration distorted from the square-plane[2,3]. The main difference between the two types lies in that the complexes of the series having a configuration distorted from the square-plane show ligand field bands with characteristic shape in the near-infrared region, while "salcomine" with square-planar configuration does not show a similar pattern, but a rather sharp band in that wavelength region.

Bis(salicylidene-2,6-xylidinato)cobalt(II), which suffers steric hindrance against forming the square-planar co-ordination around a cobalt(II) ion, shows absorption spectrum, similar to those of bis(salicylidene-alkyliminato)-cobalt(II) complexes. Moreover, all the compounds with a substituent on the carbon atom in the 2-position show absorption spectra which are similar to each other, having the main features observed for bis(salicylidene-alkyliminato)-cobalt(II) complexes. The spectra of these compounds, however, are different from the spectrum of "salcomine". It is concluded, therefore, that all these compounds synthesized in the present study, as well as bis(salicylidene-methyliminato)cobalt(II), have a configuration distorted from the square-plane.

It is concluded in a similar way that bis(salicylidene-anilinato)cobalt(II) is also distorted from the square-planar co-ordination, since the compound shows ligand field bands with features similar to those of bis(salicyl-



(I)

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

idene-2, 6-xylidinato)cobalt(II). In the former there is only slight steric hindrance between the hydrogen atom in the 2-position and the oxygen atom of the neighboring ligand. The favorable condition in energy, together with this slight steric hindrance, may be one of the main factors which give rise to the distortion from the square-planar co-ordination in this type of compounds.

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