

The Effect of Monodentate Ligands on the Structure of Co(II) Complex with a Tridentate Schiff Base

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A tridentate Schiff base, *o*-carboxy *N*-phenylsalicylaldimine, along with a number of monodentate ligands produced three types of cobalt(II) complexes, $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})\text{X}_2 \cdot 2\text{H}_2\text{O}$, where X=pyridine or α -picoline, $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})\text{X}$, where X=pyridine or picolines (α , β and γ) and $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})2\text{H}_2\text{O}$. The apparently quadri-coordinated complexes appear to have octahedral structures where the carboxyl group of Schiff base acts as a bidentate ligand. The dipyridine and the dipicoline (α) complexes are also octahedral but their structures differ from one another as revealed by IR and TG studies.

THE effect of different monodentate ligands on the stereochemistry of nickel(II) and copper(II) complexes of the tridentate Schiff base, anthranilosalicylaldimine, was discussed in our earlier communications^{1,2}. Similar studies have been made with cobalt(II) and are reported in the present paper.

Three different types of complexes have been isolated. The apparently quadri-covalent complexes are formed with pyridine, α -, β - and γ -picolines. The only apparently penta-coordinated complex that could be isolated, has the empirical formula $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})2\text{H}_2\text{O}$. Another group of complexes that has been prepared, may be represented as $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})\text{X}_2 \cdot 2\text{H}_2\text{O}$, where X=pyridine or α -picoline. However, with β - and γ -picolines the last type could not be isolated. Attempts to prepare cobalt(II) complexes with monodentate ligands, such as ammonia and different alkylamines, were equally unsuccessful due to the oxidation of the metal ion.

The magnetic moments of the complexes indicate them to be of the spin-free type and such values suggest an octahedral stereochemistry, though in the cases of quadri-covalent complexes with γ -picoline, β -picoline and pyridine, such values are in the border line of tetrahedral and octahedral configuration. The electronic absorption spectra of the complexes could not be taken due to their low solubility in all non-coordinating solvents and the reflectance spectra could not be obtained due to non-availability of such arrangements in this laboratory. However, the infra-red spectra agree with the octahedral structure. In the apparently quadri-coordinated complexes the asymmetric stretching frequency of the carboxyl group has been observed below 1600 cm^{-1} confirming the bridging character of such group as observed earlier^{1,2}. Further coordination probably occurs through the hydroxyl oxygen as in case of nickel(II) complexes¹. There is a significant difference in the IR spectra of two compounds, $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})\text{X}_2 \cdot 2\text{H}_2\text{O}$ where X=pyridine or α -picoline. One of the oxygens of the carboxyl group is free, where X= α -picoline ($\nu\text{COO}^- =$

1627 cm^{-1}), but where X=pyridine, the carbonyl oxygen is involved in coordination as the carboxyl stretching frequency is at 1607 cm^{-1} . This lowering of νCOO^- in the latter complex may also be due to the interaction of carbonyl oxygen with a hydrogen atom of one of the water molecules by hydrogen bonding. Hence, whether both the oxygens of the carboxyl group has taken part in coordination with two metal atoms forming a bridge cannot be said definitely. But it is certain that these compounds, though octahedral have somewhat different structures. This is further confirmed by their thermolysis curves (Fig.1). This

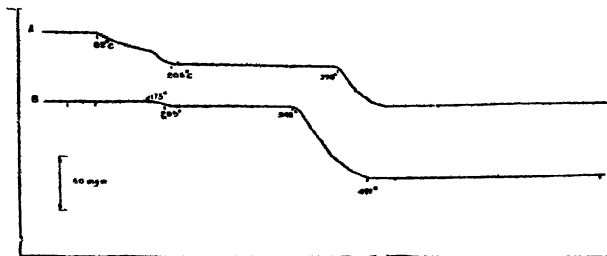


Fig. 1. Thermolysis curves.
A- $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})2\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$
B- $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})2\text{C}_5\text{H}_7\text{NCH}_3(\alpha) \cdot 2\text{H}_2\text{O}$

mode of pyrolysis is quite different. The dipyridine compound (A) loses the pyridine and water molecules simultaneously with the ultimate formation of $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})$ just above 200° , whereas that with α -picoline (B) loses only the water molecules above 175° and above 200° forms an intermediate corresponding to the formula $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})2\text{C}_5\text{H}_7\text{NCH}_3(\alpha)$, which above 348° decomposes completely to CoO.

Experimental

Preparation of the complexes

1. Diaquo *o*-Carboxy-*N*-phenylsalicylaldimine cobalt(II) :

An alcoholic solution of the Schiff base (0.01

mole) was refluxed for about 2 hr. with an aqueous solution of cobalt acetate (0.01 mole). The resulting light yellow coloured complex was filtered and washed thoroughly with alcohol and dried in the air. The complex is insoluble in all polar and non-polar organic solvents (Found : Co, 17.51 ; N, 4.04 ; C, 50.17 and H, 4.04 percent. Calc. for $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N}) 2\text{H}_2\text{O}$; Co, 17.64 ; N, 4.19 ; C, 50.26 and H, 3.89 percent). μ_{eff} , 5.40 B.M.

2. *o*-Carboxy-*N*-phenylsalicylaldimine cobalt(II) dipyridine dihydrate :

2.5g (0.01 mole) of the Schiff base were dissolved in about 25 ml of hot pyridine. To it was then added a solution of cobalt acetate, 2g (0.01 mole) in water (25 ml), and the mixture was refluxed on a steam bath for about 1 hr. The supernatant water was decanted off and the viscous liquid was dissolved in acetone. To this solution, water was added drop by drop till it became turbid. The solution was then made clear by adding a minimum quantity of acetone and then cooled, when deep orange crystals separated. These were filtered, washed with aqueous acetone and dried in air. The complex is very slightly soluble in ethanol, acetone, chloroform, carbon tetrachloride, benzene and dioxan. (Found : Co, 12.02 ; N, 8.41 ; C, 58.27 and H, 4.82 percent. Calc. for $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N}) 2 \text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$; Co, 11.98 ; N, 8.53 ; C, 58.51 and H, 4.67 percent). μ_{eff} , 4.99 B.M.

3. *o*-Carboxy-*N*-phenylsalicylaldimine cobalt(II) pyridine :

The viscous liquid as obtained in 2, was kept in a vacuum desiccator under suction for about 12 hr. The semi-solid mass thus obtained was dissolved in chloroform and then to it an excess of ligroin (60°-80°) was added when a yellow solid separated. This was filtered, washed with ligroin and dried. The complex was found to be slightly soluble in ethanol, acetone, chloroform, benzene, dioxan and pyridine (Found : Co, 15.51 ; N, 7.26 ; C, 60.08 and H, 3.92 percent. Calc. for $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N}) \text{C}_5\text{H}_5\text{N}$; Co 15.63 ; N, 7.43 ; C, 60.45 and H, 3.71 percent), μ_{eff} , 4.83 B.M.

4. *o*-Carboxy-*N*-phenylsalicylaldimine cobalt(II) di- α -picoline dihydrate :

2.5g (0.01 mole) of the Schiff base were dissolved in about 50 ml of hot α -picoline. To it was then added an aqueous solution (25 ml) of cobalt acetate (2g). The mixture was heated on a steam bath for about 1 hr. and then filtered. To the filtrate water was added when the solution became just turbid. This was then made clear by adding a minimum quantity of acetone and kept for a few days. The deep

brown crystals were filtered, washed with water and then dried in air. It is slightly soluble in ethanol, acetone, chloroform, benzene and dioxan. (Found : Co, 11.20 ; N, 7.94 ; C, 60.15 and H, 5.27 percent. Calc. for $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N}) 2\text{C}_5\text{H}_4\text{NCH}_3(\alpha) 2\text{H}_2\text{O}$; Co, 11.33, N, 8.07 ; C, 59.98 and H, 5.19 percent). μ_{eff} , 5.06 B.M.

5. *o*-Carboxy-*N*-phenylsalicylaldimine cobalt(II) α -picoline :

The Schiff base (2.5g), dissolved in about 30 ml of hot α -picoline, was heated on a steam bath for about half an hour with an aqueous cobalt acetate solution (2g in 25 ml). The light yellow compound, separated thereby, was filtered, washed thoroughly with water and dried in air. The complex is slightly soluble in ethanol, acetone, benzene, chloroform and dioxan. (Found : Co, 15.19, N, 7.21 ; C, 60.96 and H, 4.21 percent. Calc. for $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N})\text{-C}_5\text{H}_4\text{NCH}_3(\alpha)$; Co, 15.08, N, 7.16 ; C, 61.35 and H, 4.09 percent). μ_{eff} , 5.05 B.M.

6. *o*-Carboxy-*N*-phenylsalicylaldimine cobalt(II) β -picoline :

The procedure followed was the same as described for monopyridine complex, excepting that β -picoline was used in place of pyridine and the refluxing period was 2 hr. The complex is slightly soluble in ethanol, acetone, carbon tetrachloride, chloroform, benzene and dioxan. (Found : Co, 15.12 ; N, 7.04 ; C, 61.21 and H, 4.18 percent. Calc. for $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N}) \text{C}_5\text{H}_4\text{NCH}_3(\beta)$; Co, 15.08 ; N, 7.16 ; C, 61.35 and H, 4.09 percent). μ_{eff} , 4.84 B.M.

7. *o*-Carboxy-*N*-phenylsalicylaldimine cobalt(II) γ -picoline :

The method of preparation was the same as described for mono- β -picoline complex, excepting that γ -picoline was used instead of β -picoline. The complex is slightly soluble in most of the organic solvents. (Found : Co, 14.97 ; N, 7.14 ; C, 61.28 and H, 4.24 percent. Calc. for $\text{Co}(\text{C}_{14}\text{H}_9\text{O}_3\text{N}) \text{C}_5\text{H}_4\text{NCH}_3(\gamma)$; Co, 15.08 ; N, 7.16 ; C, 61.35 and H, 4.09 percent). μ_{eff} , 4.77 B.M.

Magnetic susceptibility, thermal analysis and infra-red spectra are measured as described earlier¹.

References :

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2. A. K. Majumdar and B. C. Bhattacharyya, *J. Inorg. Nuclear Chem.*, 1968, 30, 1116.