

## Structure and Derivatographic Study of Co(II) Complexes of Salicylic Acid and Thiosalicylic Acid

RAJ RANJAN JHA

*Department of Chemistry Ranchi University Ranchi, 834-008, India*

Bis(salicylato) tetraaquo cobalt(II) and bis(thiosalicylate) diaquo cobalt(II) complexes have been prepared by mixing basic cobalt carbonate with salicylic acid and thiosalicylic acid in 1 : 2 molar ratio. The complexes have been characterised by elemental analysis, IR, UV and visible reflectance spectra and derivatographic study (DT, DTA and TGA). The structure of bis(salicylato) tetraaquo cobalt(II) has been also confirmed by X-ray analysis.

### INTRODUCTION

A survey of literature shows that thermal decomposition of Co(II) complexes with salicylic acid and thiosalicylic acid have not been studied so far, though the complexes of salicylic acid and thiosalicylic acid with Co(II) are known and studied by a number of workers.<sup>1-7</sup> Because of various biological applications of salicylates and thiosalicylates, in this paper we report the derivatographic studies of bis(salicylato) tetraaquo cobalt(II) and bis(thiosalicylato) diaquo cobalt(II) in static air with the heating rate of 8°/min. The structures of both the complexes are further discussed by magnetic measurement, UV and visible reflectance spectra and IR spectra. The structure of bis(salicylato) tetraaquo cobalt(II) has been confirmed by X-ray. The oxidation of salicylate complex was carried out in 12 N sulfuric acid medium with acid dichromate and thiosalicylate complex in alkaline medium with permanganate.

### EXPERIMENTAL

The complexes have been prepared by treating basic cobalt carbonate with salicylic acid and thiosalicylic acid in 1 : 2 molar ratio as reported earlier<sup>8,9</sup>. In case of thiosalicylic acid, dioxane was used as a solvent. In case of cobalt salicylate light pink crystals of the complex separated out and in case of thiosalicylate dark pink (violet pink) amorphous products were obtained. The complexes obtained were quite stable in air. The chemical analysis<sup>10</sup> of the complexes corresponds with composition  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  and  $[\text{Co}(\text{SC}_6\text{H}_4\text{COOH})_2(\text{H}_2\text{O})_2]$  respectively.

	Found (Calculated)			
	Co	S	C	H
[Co(HOC <sub>6</sub> H <sub>4</sub> COO) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]	14.37 (14.57)	–	41.40 (41.18)	4.48 (4.44)
[Co(SC <sub>6</sub> H <sub>4</sub> COOH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	14.50 (14.75)	15.10 (16.00)	40.20 (42.00)	4.10 (3.50)

The stages of oxidation were followed potentiometrically<sup>11</sup> using bright platinum electrode. The concentrations were so chosen that 10 mL of complex solution required 10 mL of oxidant for complete oxidation to CO<sub>2</sub> stage. The results of oxidation are shown in Table 1 and 2.

TABLE-1

[H<sub>2</sub>SO<sub>4</sub>] = 12 N  
Cell 10 mL = M/560 [Co(HOC<sub>6</sub>H<sub>4</sub>COO)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]  
Oxidant = M/60 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

Temp (°C)	Time (h)	Position of inflexion in mL	No. of electron changes	Nature of inflexion
Room temp.	3	4.2	12	V. Sharp
Room temp.	24	6.4	18	V. Sharp
Room temp.	96	7.8	22	V. Sharp
90	3	8.6	24	V. Sharp
90	9	9.2	26	V. Sharp
90	15	9.8	28	V. Sharp

TABLE-2

KOH = 0.1. N.  
Cell 10 mL = [Co(SC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]  
Oxidant = M/30 KMnO<sub>4</sub>

Temp (°C)	Time (h)	Position of inflexion in mL	No. of electron changes	Nature of inflexion
Room temp.	3	0.3	1	Sharp
Room temp.	96	6.3	1	Sharp
60	3	1.2	4	Sharp
60	6–9	1.8	6	Sharp

The IR spectra was recorded on a Perkin-Elmer model No 221. The derivatographic study was made on a Paulik, Paulik and Erdey model manufactured by M/s M.O.M. (Hungarian Optical Works). The spectrophotometric study was carried out on Hilger and Watt unspeak spectrophotometer Model No. 700. For X-ray diffraction analysis good single crystal was selected by observing extinction under a polarised microscope. Oscillation rotation and Weissenberg photographs were taken with CuK<sub>α</sub> radiation to determine unit cell, space group

and cell contents. The final structure was determined by three-dimensional X-ray diffraction data by heavy atom technique. Crompton potentiometer was used to record the e.m.f. of each mixture.

## RESULTS AND DISCUSSION

The interaction of cobalt(II) carbonate with excess salicylic acid in aqueous solution at reflux temperature resulted in the formation of  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  while with thiosalicylic acid  $[\text{Co}(\text{SC}_6\text{H}_4\text{COOH})_2(\text{H}_2\text{O})_2]$  was isolated in dioxane.

To support the proposed structure and nature of bond in the complexes, magnetic susceptibility measurement and UV and visible spectral studies of the complexes have been made. The magnetic susceptibility measurement of  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  is 5.27 B.M. at room temperature unambiguously support octahedral structure of the complex. The magnetic moment value of  $[\text{Co}(\text{SC}_6\text{H}_4\text{COOH})_2(\text{H}_2\text{O})_2]$  is 3.68 B.M. at room temperature is quite low for spin-free octahedral as well as tetrahedral cobalt(II) complexes. However, it occurs in the range of octahedral cobalt(II) complex with spin state of cobalt(II) atom. The observation is quite similar to a number of octahedral cobalt(II) complexes with sulphur containing ligands.

The electronic reflectance spectra of  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  exhibits two weak bands located at  $18200\text{ cm}^{-1}$  and  $22900\text{ cm}^{-1}$  (shoulder) attributed to  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  and  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$  transitions of octahedrally situated cobalt(II) atom. As expected for two electron transition  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{F})$  the transition is weak since it is generally unobserved in majority of octahedral cobalt(II) complexes. The thiosalicylic acid complex  $[\text{Co}(\text{SC}_6\text{H}_4\text{COOH})_2(\text{H}_2\text{O})_2]$  does not exhibit definite band in visible region; probably the d-d transitions are observed in charge transfer transition which arises from Co—S bonding. The darkening of complex further suggests Co—S bonding in  $[\text{Co}(\text{SC}_6\text{H}_4\text{COOH})_2(\text{H}_2\text{O})_2]$  complex.

The infrared spectral studies of the complexes were recorded in the region  $4000\text{--}650\text{ cm}^{-1}$ . The IR spectrum of salicylic acid displays a medium and broad band at  $3240\text{--}2580\text{ cm}^{-1}$  due to —OH phenolic and —OH of carboxylic group (COOH). The position of the band in nujol mull disc indicates appreciable hydrogen bonding in the free ligand. In complex  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  the broad and medium band between  $3480\text{--}3200\text{ cm}^{-1}$  can be attributed to combination of  $\nu(\text{H}_2\text{O})$ ,  $\nu(\text{OH})$  phenolic group of salicylic acid. The  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$  of salicylic acid are observed at  $1659\text{ cm}^{-1}$ ,  $1682\text{ cm}^{-1}$  and  $1292\text{ cm}^{-1}$  (s) respectively. The phenolic —OH group out-of-plane bending band is observed at  $1388\text{ cm}^{-1}$  in nujol mull and at  $1403\text{ cm}^{-1}$  in benzene<sup>12-14</sup>. In cobalt(II) complex in nujol mull the band at  $1388\text{ cm}^{-1}$  is not affected appreciably, thus indicating that phenolic OH is not involved in bond. The  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$  are affected appreciably and observed at  $1385\text{--}1370\text{ cm}^{-1}$  respectively indicating that carboxylic group oxygen molecules are involved in bonding the carboxylic group (OH); the out-of-plane bending band located at  $1404\text{ cm}^{-1}$  in free acid in KBr disc disappears in complex suggesting the deprotonation of

carboxylic group (COOH) hydrogen. A medium and broad band at  $815\text{ cm}^{-1}$  attributable to  $\text{H}_2\text{O}$  deformation vibration supports the coordination of the  $\text{H}_2\text{O}$  in  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$ .

The comparison of IR spectra of thiosalicylic acid and its complex  $[\text{Co}(\text{SC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  as nujol mull suggests the bonding of ligand molecule both through carboxylic oxygen and thiol sulphur. The free ligand displays (S—H) band at  $2520\text{ cm}^{-1}$  which disappears in complex  $[\text{Co}(\text{SC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$ . The (OH) vibration of (COOH) group is observed as broad band between  $3100\text{--}2800\text{ cm}^{-1}$  which is retained in complex and observed as broad band between  $3400\text{--}2800\text{ cm}^{-1}$  due to combination with  $\nu(\text{OH})$  vibration of coordinated water molecules. The  $\nu(\text{COO})$  vibrations of ligand located at  $1670\text{--}1265\text{ cm}^{-1}$  are observed at  $1570\text{--}1370\text{ cm}^{-1}$  indicating the involvement of COO group in coordination. Further the OH out-of-plane bending band of COOH group ( $1408\text{ cm}^{-1}$ ) is not effected appreciably suggesting that (COOH) proton has been retained in the complex. The (C—S) band of the ligand assigned at  $700\text{ cm}^{-1}$  also shifts to lower frequency and observed at  $650\text{ cm}^{-1}$  supporting the bending of thiol sulphur in the complex.

The derivatographic studies of both the complexes were made with heating rate of  $8^\circ/\text{min}$  in static air between  $30^\circ$  to  $800^\circ\text{C}$ .

The combined DTG, DTA and TGA curve of a sample of  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  (Table-3) indicates that dehydration starts at  $80^\circ\text{C}$  and ends at  $150^\circ\text{C}$  as indicated by DTG curve. This step is shown by an endothermal peak in DTA. The inflexion point of the endotherm is at  $140^\circ\text{C}$ . This is also a stable point in TGA curve. The loss in weight at this stage is of 107 mg (required loss for  $4\text{H}_2\text{O}$  molecule is 107 mg). The loss in weight in TGA curve indicates that all the water molecules associated with the complex are of similar nature.

TABLE-3  
DERIVATOGRAPHIC RESULT OF  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$   
Initial wt = 600 mg

Position of peak in the DTG curve ( $^\circ\text{C}$ )	Loss in weight in TGA curve (mg)	Expected intermediate product	Nature of peak in DTA curve ( $^\circ\text{C}$ )
80–150	107	$[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2]$	Endo 140
270–325	307	$[\text{Co}(\text{OC}_6\text{H}_4\text{COO})]$	Endo 310
340–470	450	$\text{CoCO}_3$	Exo 415 Endo 470
530–590	500	$\text{CoO}$	Endo 570
600–665	480	$\text{Co}_3\text{O}_4$	Exo 640

The second step of loss in weight starts at  $270^\circ\text{C}$  and ends at  $325^\circ\text{C}$ . This step is shown by an endothermal peak in DTA curve. The inflexion point is located at  $310^\circ\text{C}$  which is also the stable point in TGA curve. The loss in weight in this step as shown by TGA curve is 200 mg indicating the elimination of one salicylic acid molecule from anhydrous complex  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2]$ . Thus the weight

of the product obtained at this stage almost corresponds with the required weight of  $[\text{Co}(\text{OC}_6\text{H}_4\text{COO})]$ .

The third stage of decomposition starts at  $340^\circ\text{C}$  and ends at  $470^\circ\text{C}$  which is indicated by a peak in DTG curve. Here two types of reaction occur; first process is exothermal and the second endothermal. The inflexion point of exothermic peak is at  $415^\circ\text{C}$  and that of endothermic peak at  $470^\circ\text{C}$ . The loss in weight in this stage is of 143 mg which is indicated by TGA curve. The product obtained at this stage corresponds with the weight of  $\text{CoCO}_3$ . The DTG curve indicates that second step of decomposition starts at  $530^\circ\text{C}$  and ends at  $590^\circ\text{C}$ . This is shown by an endothermal peak in D.T.A. curve. The endothermal peak starts at  $535^\circ\text{C}$  and ends at  $590^\circ\text{C}$ . The inflexion point of the peak is at  $570^\circ\text{C}$ . The loss in weight is 50 mg. The loss in weight indicates that the product obtained has a composition  $\text{CoO}$ .

The last step is due to gain in weight. This is due to the fact that  $\text{CoO}$  is oxidised to  $\text{Co}_3\text{O}_4$ . The gain in weight in this range is of 20 mg. The product is formed by an exothermal reaction. This step starts at  $600^\circ\text{C}$  and ends at  $665^\circ\text{C}$ . The inflexion point of the exotherm is at  $640^\circ\text{C}$ . The formation of final product as  $\text{Co}_3\text{O}_4$  has been confirmed by analysis of cobalt content in the residue.

Thermal behaviour of  $[\text{Co}(\text{SC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_2]$  is similar to  $[\text{Co}(\text{OHC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$ . The results of derivatographic studies of  $[\text{Co}(\text{SC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_2]$  is summarized in Table-4.

TABLE-4  
DERIVATOGRAPHIC RESULT OF  $[\text{Co}(\text{SC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_2]$   
Initial wt. = 500 mg

Position of peak in the DTG Curve	Loss in weight in mg	Expected intermediate product	Nature of peak in DTA curve
80–180°C	44 mg	$[\text{Co}(\text{SC}_6\text{H}_4\text{COO})_2]$	Endo 165
310–335°C	240 mg	$[\text{Co}(\text{SC}_6\text{H}_4\text{COO})]$	Endo 350
360–420°C	343 mg	Product not confirmed	Exo 380 Endo 420
420–580°C	368 mg	Product not confirmed	Endo 480 Exo 580
580–630°C	406 mg	$\text{CoO}$	Endo 630
630–665°C	395	$\text{Co}_3\text{O}_4$	Exo 650

### X-ray Analysis

The structural analysis of  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  indicates that water molecules are coordinated to the central cobalt(II) atom and cobalt(II) atom is in octahedral environment with OH symmetry. The free phenolic —OH group of salicylic acid is involved in hydrogen bonding with free COO oxygen of carboxylic group. The detailed X-ray structure is discussed below.

The  $[\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4]$  crystal was found to be monoclinic with the following cell parameters:

$$a = 6.84, \quad b = 24.25, \quad c = 5.18, \quad \alpha = \gamma = 90, \quad \beta = 107.4^\circ$$

Space group  $P_{21/c}$ ; unit cell volume =  $820.4 \text{ \AA}^3$ ;  $P = 1.66$ .

No. of formulae within the unit cell  $Z = 2$ .

The density of the crystal was determined by the floatation method with a mixture of toluene and bromoform; the observed density was found to be 1.66 which gives a unit cell content  $M_n = 820.4$ . The calculated density, assuming  $Z = 2$ , comes to be 1.65 which is in excellent agreement with the observed density.

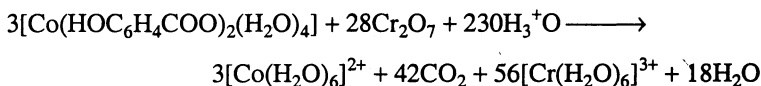
The unit cell contains 2 asymmetric units of the formula  $[\text{Co}(\text{C}_6\text{H}_4\text{OHCOO})_2(\text{H}_2\text{O})_4]$  determined by 3-dimensional X-ray diffraction data by heavy atom technique. The metal ion occupies the specific positions 0, 0, 0, and 0, 1/2, 1/2. Here the metal atom is linked with six oxygen atoms: two oxygens from two carboxylic groups and four oxygens from four water molecules. The metal and oxygen bond distance and bond angle are tabulated below:

Co-w <sub>1</sub>	2.13 (i)	w <sub>1</sub> -Co-w <sub>2</sub>	93.0°
Co-w <sub>2</sub>	2.10 (i)	O <sub>2</sub> -Co-w <sub>1</sub>	93.5°
Co-O <sub>2</sub>	2.09 (i)	O <sub>2</sub> -Co-w <sub>2</sub>	90.1°

These bond lengths and bond angles are with one salicylic acid molecule; with the other it is same. In this complex the metal ion has sixfold coordination with an average distance of 2.13.

### Oxidation

With acid dichromate the overall oxidation of bis(salicylate) tetraaquocobalt(II) can be represented by the stoichiometric equation.



The very sharp inflexion obtained at 4.2 mL after 3h storage at room temperature corresponds to 12 electron abstraction stage per mole salicylic acid and IR spectrum indicates absence of aromatic ring. The oxidation products of salicylic acid at this stage were identified to be maleic acid and mesooxalic acid in equimolar proportion; other intermediates identified were mesotartaric acid on 24 h room temperature storage (inflexion at 6.2 mL corresponding to 18 electron abstraction stage). On prolonged storage at room temperature (144 h) hydroxymalonic acid is formed which accounts for very sharp inflexion at 7.8 mL (corresponding to 22 electron abstraction stage). Most of these intermediates were in the form of Cr(III) complexes. At elevated temperatures further oxidation takes place and ultimately carbon dioxide is formed on heating for 15 h at 90°C through intermediate formation of glyoxalic acid (3 h heating giving inflexion at 8.6 mL corresponding to 24 electron abstraction stage) and formic acid (9 h at 95°C giving inflexion at 9.4 mL corresponding to 26 electron abstraction stage).

With alkaline permanganate, the oxidation of  $[\text{Co}(\text{SC}_6\text{H}_4\text{COOH})_2(\text{H}_2\text{O})_2]$  is slow. The oxidation only takes place when heated at 60°C. Only 1.8 mL oxidant is consumed corresponding to 6 electron abstraction stage. The product obtained at this stage in *o*-sulfobenzoic acid.

## REFERENCES

1. K. Garbett and R.D. Gillard, *J. Chem. Soc(A)*, 979 (1968).
2. A.G. Beaumont, R.D. Gillard and J.R. Lyons, *J. Chem. Soc. (A)*, 1361 (1971).
3. R.D. Gillard, J.R. Lyons and P.R. Mitchell, *J. Chem. Soc. (Dal. Trans.)*, 233 (1973).
4. G.A. Barbieri, *Atti. Accad. Lincei*, **25**, 75 (1917).
5. J. Plaquin and C. Vergneak, *Bull. Soc. Khim. France*, 757 (1951).
6. M. Bostelskye and I. Ber-Gadda, *Bull. Soc. Khim. France*, 687 (1953).
7. N. Matsuoko, Y. Shimur and T. Tsuchida, *Nippo Kigaku Zasshi*, 1637 (1961).
8. H.C. Mishra, R.R. Jha and S.N. Mukherjee, *J. Indian Chem. Soc.*, **56**, 525 (1979).
9. H.C. Mishra and R.R. Jha, *J. Indian Chem. Soc.*, **57**, 769 (1980).
10. B.P. Gyani and S.N. Prasad, *J. Indian Chem. Soc.*, **32**, 313 (1955).
11. M.R. Gajendragad and U. Agarwala, *J. Inorg. Nucl. Chem.*, **77**, 2429 (1975).
12. J.H.S. Green, W. Kynaston and A.L. Lindsey, *Spectrochim Acta*, **17**, 486 (1961).
13. F.E. Murray and S. Sundaram, *Can J. Chem.*, **39**, 1625 (1961).
14. C.K.W. Brooks, G. Eglinton and J.F. Forman, *Canad J. Chem.*, **39**, 661 (1961).

(Received: 17 February 2001; Accepted: 7 April 2001)

AJC-2314