

# Magnetic and Spectral Studies on Cobalt(II) Complexes of Salicylaldehyde Schiff base of Isonicotinoyldithiocarbazic Acid

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## ABSTRACT

New cobalt(II) dithiocarbazates of the general formula  $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_n$  (IN-DtczH-Sal = salicylaldehyde Schiff base of isonicotinoyldithiocarbazic acid; X = Cl, Br,  $\text{ClO}_4$ ,  $\text{NO}_3$ ,  $\text{CH}_3\text{COO}$  for  $n = 2$ , X =  $\text{SO}_4$ ,  $\text{C}_2\text{O}_4$ ,  $\text{CO}_3$  for  $n = 1$ ) have been prepared and investigated by elemental analyses, molar conductance measurements, infrared and electronic spectral and room temperature and variable temperature magnetic susceptibility measurements. All the complexes have NS linkage of the ligand. The magnetic and spectral studies suggest that the complexes, viz.  $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_2$  (X = Cl,  $\text{CH}_3\text{COO}$ ,  $\text{NO}_3$ ) are square planar, while the temperature dependent magnetic behaviour of the complexes  $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_n$  (X = Br,  $\text{ClO}_4$  when  $n = 2$ ; X =  $\text{SO}_4$ ,  $\text{C}_2\text{O}_4$  when  $n = 1$ ) indicate square planar – tetrahedral equilibrium. Additionally the magnetic behaviour of the two complexes with sulphate and oxalate as the counter anions has also been attributed to the presence of intermolecular superexchange antiferromagnetic interactions in a sulphato/oxalato bridged dimeric structure. The  $\text{Co}(\text{IN-DtczH-Sal})_2\text{CO}_3$  complex exhibits octahedral geometry, with carbonate anion also taking part in bonding.

## INTRODUCTION

Sulphur-nitrogen chelating agents derived from Schiff bases of dithiocarbazic acids and their transition metal complexes have been the subject of many studies<sup>1-5</sup> mainly because of their interesting physico-chemical properties and potentially beneficial biological activities. The dithiocarbazate and its substituted derivatives have received much attention because (i) they provide an interesting series of ligands whose properties can be greatly modified by introducing different organic substituents, thereby causing a variation in the ultimate donor properties, (ii) the interaction of these donors with metal ions gives complexes of different donicity, geometry and hence physico-chemical properties, and (iii) these complexes are potentially biologically active. Schiff bases of dithiocarbazic acids with thiol groups have been reported to generally oxidize cobalt(II) to cobalt(III)<sup>6,7</sup>. As part of our on-going work on metal dithiocarbazates, we report here the magnetic and spectroscopic characterization of cobalt(II) complexes of the NS bonded bidentate Schiff base ligand formed by the condensation of salicylaldehyde with isonicotinoyldithiocarbazic acid. Oxidation of even trace amounts of cobalt(II) to cobalt(III) has been ruled out with the ligand of the present study.

## MATERIALS AND METHODS

Isoniazid, carbon disulphide, salicylaldehyde, cobalt(II) salts, methanol and ethanol, all from Merck were of analytical grade and used as such. IN-DtczH-Sal Schiff base ligand was prepared according to the method described elsewhere<sup>8</sup>.

### Preparation of complexes

**$[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_2$  (X = Cl, Br,  $\text{NO}_3$ ,  $\text{ClO}_4$ ):** Schiff base IN-DtczH-Sal (2.0 g, 6.30 mmol) was dissolved in ethanol (50 ml). A solution of cobalt salt,  $\text{CoX}_2 \cdot 6\text{H}_2\text{O}$  (0.75 g, 3.15 mmol for X = Cl; 1.03 g, 3.15 mmol for X = Br; 0.92 g, 3.15 mmol for X =  $\text{NO}_3$  and 1.15 g, 3.15 mmol for X =  $\text{ClO}_4$ ) in ethanol (30 ml) was added to it with stirring, in small portions after successive intervals of about 10-15 minutes, in a total period of about 2 hours. The reaction was carried out at 40-45 °C. Though the solid coloured product separates out immediately, yet the reaction mixture was stirred for another 1 hour to ensure the completion of the reaction. The solid product obtained (green when X = Cl and brown when X = Br,  $\text{NO}_3$

and  $\text{ClO}_4$ ) was filtered, washed with ethanol, diethyl ether and then dried in air. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator.

**[Co(IN-DtczH-Sal)] $_2$ X $_n$  (X = CH $_3$ COO when n = 2 and X = SO $_4$  when n = 1):** To a continuously stirred methanolic solution (50 ml) of IN-DtczH-Sal Schiff base (2.0 g; 6.30 mmol), was added methanolic solution (40 ml) of cobalt salt, CoX $_n$ .xH $_2$ O (0.78 g, 3.15 mmol for X = CH $_3$ COO, n = 2, x = 4 and 0.88 g, 3.15 mmol for X = SO $_4$ , n = 1, x = 7), in small portions after successive intervals of about 10-15 minutes, in a total period of about 2 hours. The reaction was carried out at 40-45 °C. Though the solid coloured product separates out immediately, yet the reaction mixture was stirred for another 1 hour to ensure the completion of the reaction. The solid product obtained (brown when X = CH $_3$ COO and orange when X = SO $_4$ ) was filtered, washed with methanol, diethyl ether and then dried in air. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator.

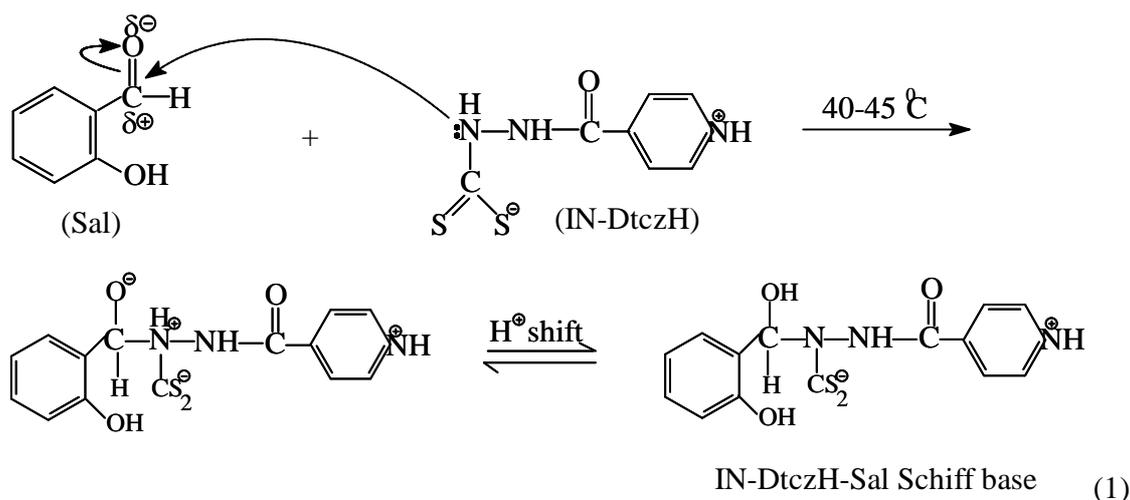
**[Co(IN-DtczH-Sal)] $_2$ X (X = C $_2$ O $_4$ , CO $_3$ ):** Slightly less than the stoichiometric amount of solid cobalt salt CoX.xH $_2$ O (0.58 g, 3.15 mmol for X = C $_2$ O $_4$ , x = 2 and 0.38 g, 3.15 mmol for X = CO $_3$ , x = 0), was added in small portions, after successive intervals of about 25 minutes in a total period of about 5 hours, to the continuously stirred ethanolic solution (50 ml) of IN-DtczH-Sal Schiff base (2.0 g, 6.30 mmol). The contents were further stirred and refluxed at 50-60 °C for about 72 hours. The solid coloured product (creamish-yellow when X = C $_2$ O $_4$  and brown when X = CO $_3$ ) thus separated was filtered through Whatman filter paper no. 541, washed with ethanol, diethyl ether and then dried in air. Final drying of the sample was done by keeping it overnight in a calcium chloride desiccator.

#### Elemental Analyses and Physical Measurements

Cobalt, chloride, bromide, oxalate and acetate contents in the complexes were determined by the methods as reported earlier<sup>9</sup>. Carbon, hydrogen, nitrogen and sulphur analysis and IR and solution electronic spectral (DMF or DMSO) and magnetic susceptibility measurements and molar conductances (10 $^{-4}$  M solutions in DMSO at 25 ± 0.1 °C) were made by the methods as described earlier<sup>10</sup>.

#### RESULTS AND DISCUSSION

The salicylaldehyde Schiff base derivative of isonicotinoyldithiocarbamic acid (IN-DtczH) was obtained by reacting hot methanolic solutions of IN-DtczH and salicylaldehyde in 1:1 stoichiometric ratio, according to the reaction (1).



The synthesis of different cobalt(II) complexes of IN-DtczH-Sal Schiff base ligand follows the general reaction (2):



X = Cl, Br, NO<sub>3</sub>, ClO<sub>4</sub> for n = 2, x = 6

X = CH<sub>3</sub>COO for n = 2, x = 4

X = SO<sub>4</sub> for n = 1, x = 7

X = C<sub>2</sub>O<sub>4</sub> for n = 1, x = 2

X = CO<sub>3</sub> for n = 1, x = 0

Cobalt(II) complexes of IN-DtczH-Sal Schiff base are highly stable coloured solids, though it is advisable to store them over anhydrous calcium chloride. The complexes are insoluble in most of the common solvents, viz. cold/hot water, methanol, ethanol, acetone, chloroform, dichloromethane and carbon tetrachloride but have some solubility in dimethylsulfoxide. All the complexes do not melt but decompose between 217-325 °C (Table 1).

#### Infrared Spectral Studies

Disappearance of strong >C=O salicylaldehyde absorption (1670 cm<sup>-1</sup>)<sup>11,12</sup> in the IN-DtczH-Sal Schiff base derivative and appearance of an additional strong absorption band at 1290 cm<sup>-1</sup>, has been attributed to the formation of C-N bond as a result of Perkin's reaction. This also finds support from the observation of

a new strong ν(C-O) absorption at 1159 cm<sup>-1</sup> due to  $\text{Ar}-\overset{\text{OH}}{\underset{|}{\text{C}}}-\text{N}$  part of the Schiff base ligand.

In the IN-DtczH-Sal Schiff base a broad band of medium intensity in the 3200-3100 cm<sup>-1</sup> range, higher than the normally observed range (3100-2700 cm<sup>-1</sup>) has been observed due to ν(N-H)<sup>13</sup> and ν(O-H) modes. The absence of ν(SH) vibrational mode at 2570 cm<sup>-1</sup> is indicative of the fact that the IN-DtczH-Sal Schiff base ligand exists in its thione form (Zwitterionic form) and not the thiol form<sup>14-16</sup>.

A strong absorption of amide group (-CONH-) in the heteroaryl dithiocarbazic acid part of the IN-DtczH-Sal Schiff base ligand at 1652 cm<sup>-1</sup> due to the ν(C=O) mode (Amide I band) does not exhibit any significant shift in all of its cobalt(II) complexes (1659-1653 cm<sup>-1</sup>) and rules out the bonding through this carbonyl group. It is difficult to interpret the region (1600-1500 cm<sup>-1</sup>) due to ν(N-H) absorption (Amide II band) because of a large number of other absorption frequencies appearing in this region.

The ν(C-N) of -CONH- (Amide III band) appears at 1408 cm<sup>-1</sup> in free IN-DtczH-Sal Schiff base, a position where free IN-DtczH shows its absorption (1410 cm<sup>-1</sup>; no change in electronic effects). While in case of all its transition metal complexes, this band has been observed in the 1445-1434 cm<sup>-1</sup> range, with a blue shift of ~24-35 cm<sup>-1</sup>, thus suggesting the coordination of the amide nitrogen atom to the metal ion with consequent strengthening of the C-N bond of the amide group. The azomethine ν(N-N) vibrational modes have been observed at 1064 and 1069-1059 cm<sup>-1</sup> for free IN-DtczH-Sal Schiff base and its metal complexes respectively. No change in its band frequency implies neutralization of the overall electronic effects of the whole ligand.

The spectra of all dithiocarbazate complexes exhibit strong absorption near 1034-1015 cm<sup>-1</sup> due to ν<sub>a</sub>(CS) vibrational mode and this absorption is either split into two or has well defined shoulders<sup>17-19</sup>. This supports the unidentate sulphur coordination associated with the NS binding mode of the IN-DtczH-Sal Schiff base ligand.

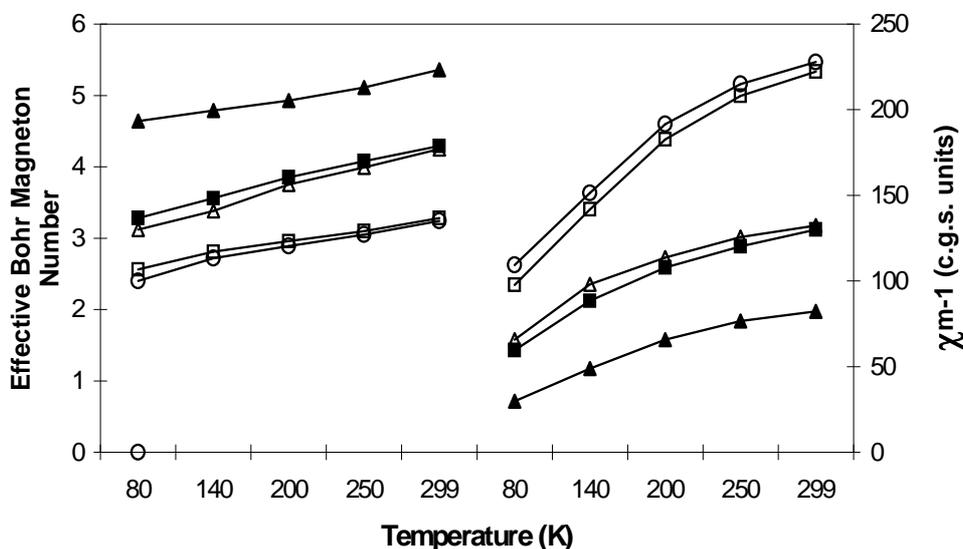
All the counteranions, viz. acetate, nitrate, perchlorate, sulphate and oxalate are not coordinated to the cobalt metal ion and exist in the ionic form with the exception of carbonate as the counter anion in Co(IN-DtczH-Sal)<sub>2</sub>CO<sub>3</sub> complex, exhibiting chelating bidentate mode of coordination (Table 2).

### Molar Conductance Studies

The molar conductance values of  $10^{-4}$  M DMSO solutions of the complexes of the general formula  $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_n$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4, \text{CH}_3\text{COO}$  for  $n = 2$ ) lie in the range  $160\text{--}178 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  corresponding to 1:2 electrolytic behaviour<sup>20</sup>. While for the complexes with  $\text{X} = \text{C}_2\text{O}_4$  and  $\text{SO}_4$  for  $n = 1$ , the molar conductance values lie in the range  $75\text{--}80 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  corresponding to 1:1 electrolytic behaviour. The  $\text{Co}(\text{IN-DtczH-Sal})_2\text{CO}_3$  complex is non-electrolytic in nature.

### Magnetic Susceptibility Studies

The room-temperature effective Bohr magneton numbers for three of the cobalt isonicotinoyldithiocarbazates,  $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_2$  ( $\text{X} = \text{Cl}, \text{CH}_3\text{COO}, \text{NO}_3$ ) range between 2.1 and 2.34 B.M. These  $\mu_{\text{eff}}$  values lie in the range corresponding to one unpaired electron for square planar stereochemistry around cobalt(II),  $d^7$  complexes. The magnetic moments for these complexes are not found to vary with temperature between 80 and 299 K. For the complexes  $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_n$  ( $\text{X} = \text{Br}, \text{ClO}_4$  when  $n = 2$ ;  $\text{X} = \text{SO}_4, \text{C}_2\text{O}_4$  when  $n = 1$ ) room-temperature magnetic moment values range between 3.24 and 4.25 B.M.. These values lie between those expected for tetrahedral ( $S = 3/2$ ) and square planar ( $S = 1/2$ ) cobalt(II) complexes: 4.4 - 4.8 B.M. and 2.1-2.8 B.M., respectively<sup>21</sup>. Also, the magnetic moment values are found to decrease with decrease of temperature to 2.4 and 3.28 B.M. respectively at 80 K (Figure 1). This may indicate the presence of a square planar-tetrahedral equilibrium. For the complex  $\text{Co}(\text{IN-DtczH-Sal})_2\text{CO}_3$ , the room-temperature  $\mu_{\text{eff}}$  value is 5.36 B.M. and is found to decrease with decreasing temperature (Figure 1). In this complex the infrared spectral study inferred bidentate NS donor behaviour of the ligand resulting into four coordination around the cobalt(II) ion, however, six coordination is achieved through bonding of the dinegative anion, i.e. carbonate resulting into bridged octahedral structure. Thus, the infrared study indicates six coordination for this complex resulting into octahedral structure.



**Fig. 1: Variation of Effective Bohr Magnetron Numbers and  $\chi_{\text{M}}^{-1}$  of**  
 $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{Br}_2$  (—○—)  
 $[\text{Co}(\text{IN-DtczH-Sal})_2](\text{ClO}_4)_2$  (—□—)  
 $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{SO}_4$  (—■—)  
 $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{C}_2\text{O}_4$  (—△—)  
 $\text{Co}(\text{IN-DtczH-Sal})_2\text{CO}_3$  (—▲—) with Temperature.

### Electronic Absorption Spectral Studies

In the solution electronic absorption spectra of three cobalt(II) complexes,  $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_2$  ( $\text{X} = \text{Cl}, \text{CH}_3\text{COO}, \text{NO}_3$ ), the four observed absorption bands are indicative of  $D_{2h}$  symmetry for the cobalt(II)  $d^7$  planar stereochemistry<sup>21</sup>. A well defined strong band occurring at  $16,990\text{-}17,800\text{ cm}^{-1}$  is assigned to the transitions  ${}^2B_{1g} \leftarrow {}^2A_g (x^2-y^2 \rightarrow xy)$  and  ${}^2B_{3g} \leftarrow {}^2A_g (xz \rightarrow xy)$ . A shoulder around  $23,255\text{-}23,365\text{ cm}^{-1}$  and another strong band around  $28,170\text{-}30,030\text{ cm}^{-1}$  are metal-to-ligand charge transfer bands. These are assigned to the  ${}^2B_{2u} \leftarrow {}^2A_g (xz \rightarrow L(\pi^*))$  and  ${}^2B_{3u} \leftarrow {}^2A_g (yz \rightarrow L(\pi^*))$  transitions respectively. In addition to the bands that appear in the  $d^8$  system, a low energy  $d-d$  band appears around  $9,300\text{-}9,500\text{ cm}^{-1}$  for the cobalt(II),  $d^7$  dithiocarbazates under study and this has been attributed to the transitions  ${}^2B_{3g} \leftarrow {}^2A_g (2b_{3g} \rightarrow 4a_g, yz \rightarrow x^2-y^2)$  and  ${}^2B_{2g} \leftarrow {}^2A_g (2b_{2g} \rightarrow 4a_g, xz \rightarrow x^2-y^2)$ . The band between  $23,255\text{-}23,365\text{ cm}^{-1}$  is of high intensity and may be due to intensity stealing phenomenon from its higher lying charge transfer band of very high intensity around  $28,170\text{-}30,030\text{ cm}^{-1}$ . The observation of four electronic spectral bands, rather than two generally observed for tetrahedral cobalt(II) complexes, and the reasonable band assignments given above suggest a square-planar geometry with  $\text{CoN}_2\text{S}_2$  central core for these complexes.

The DMSO solution electronic absorption spectra of  $[\text{Co}(\text{IN-DtczH-Sal})_2]\text{X}_n$  ( $\text{X} = \text{Br}, \text{ClO}_4$  when  $n = 2$ ;  $\text{X} = \text{SO}_4, \text{C}_2\text{O}_4$  when  $n = 1$ ) complexes exhibit four absorption bands in the regions  $\sim 27,625\text{-}29,675$ ;  $23,040\text{-}24,450$ ;  $17,640\text{-}18,870$  and  $8,420\text{-}8,500\text{ cm}^{-1}$ . Since the two strong bands generally observed for tetrahedral cobalt(II) complexes lie in the same energy region as the low energy bands for the square planar stereochemistry of cobalt(II), the bands around  $17,640\text{-}18,870$  and  $8,420\text{-}8,500\text{ cm}^{-1}$  observed in the spectra of present cobalt(II) complexes may be considered the bands which are characteristic of the tetrahedral as well as square planar geometry around cobalt(II) ion. Therefore, the electronic transitions which give rise to these bands may be described, in the tetrahedral and square planar geometry of cobalt, as:  $v_3[{}^4T_1(\text{P}) \leftarrow {}^4A_2(\text{F})]$ ,  ${}^2B_{1g} \leftarrow {}^2A_g (x^2-y^2 \rightarrow xy)$ ,  ${}^2B_{3g} \leftarrow {}^2A_g (xz \rightarrow xy)$  and  $v_2[{}^4T_1(\text{F}) \leftarrow {}^4A_2(\text{F})]$ ,  ${}^2B_{3g} \leftarrow {}^2A_g (2b_{3g} \rightarrow 4a_g, yz \rightarrow x^2-y^2)$ ,  ${}^2B_{2g} \leftarrow {}^2A_g (2b_{2g} \rightarrow 4a_g, xz \rightarrow x^2-y^2)$  respectively. The additional absorptions in the higher energy region are characteristic of the square planar geometry of cobalt(II). The band at  $23,040\text{-}24,450\text{ cm}^{-1}$  is assigned to  ${}^2B_{2u} \leftarrow {}^2A_g (xz \rightarrow L(\pi^*))$  and the strong band at  $\sim 27,625\text{-}29,675\text{ cm}^{-1}$  to the  ${}^2B_{3u} \leftarrow {}^2A_g (yz \rightarrow L(\pi^*))$  metal-to-ligand charge transfer transitions for the square planar geometry of the complexes. The electronic spectra, therefore, appear to suggest that for the cobalt(II) dithiocarbazates, the two geometries - square planar and tetrahedral - are present simultaneously.

The DMSO solution electronic absorption spectrum of the  $\text{Co}(\text{IN-DtczH-Sal})_2\text{CO}_3$  complex exhibits two bands around  $11,200\text{ cm}^{-1}$  in the near infrared region and around  $23,200\text{ cm}^{-1}$  in the visible region. These have been assigned to the  $v_1[{}^4T_{2g}(\text{F}) \leftarrow {}^4T_{1g}(\text{F})]$  and  $v_3[{}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\text{F})]$  transitions respectively. The band in the visible region has a shoulder around  $14,925\text{ cm}^{-1}$  on low-energy side assigned to the  $v_2[{}^4A_{2g}(\text{F}) \leftarrow {}^4T_{1g}(\text{F})]$  transition and it shows a sign of splitting. The observation of the sign of splitting for the shoulder around  $14,925\text{ cm}^{-1}$  can be attributed to the spin-orbit coupling, vibrational broadening, low symmetry components to the ligand field or transitions to doublet states<sup>21,22</sup>.

The ligand field experienced for the high spin octahedral cobalt(II) in its  $\text{Co}(\text{IN-DtczH-Sal})_2\text{CO}_3$  complex has been calculated in terms of the ligand field parameter,  $10Dq = 12,735\text{ cm}^{-1}$  and the interelectronic repulsion parameter,  $B = 903.22\text{ cm}^{-1}$  (free ion value for  $\text{Co}^{+2}$  ( $B_0 = 1,120\text{ cm}^{-1}$ ) using Tanabe Sugano diagram<sup>23</sup>. The range of  $B$  and  $10Dq$  values match with those reported earlier.

A rationale, based upon electronegativities, polarisabilities, polarising power, permanent dipole moment and  $\pi$ -bonding characteristics, may be made for the series of ligand groups of the secondary coordination sphere. Thus, presence of different types of anions in the secondary coordination sphere influences the physical properties because of the mismatching of ion size (charge), shape and  $\pi$  bonding; structural effects, e.g. Jahn-Teller effect and radius changes, and thermodynamic effects, e.g. CFSE, become important in perturbing the balance between the different stereochemistries when different types of the ions are present in secondary coordination sphere. This "anion effect" probably arises from a combination of factors related to crystal structure (e.g. mismatching of ion size and shape, imbalance of attractive power, etc.) and to molecular geometry.

**Table 1: Elemental Analytical Data and Physical Data of IN-DtczH-Sal Schiff Base and its Cobalt (II) Complexes**

Sr. No.	Compound (Composition) Formula weight	Elemental Analyses Found (Calc.) (%)						Yield (%)	Decomp Temp. (°C)	Colour
		C	H	N	S	M	X			
1.	IN-DtczH-Sal (C <sub>14</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> S <sub>2</sub> ) 317.28	52.49 (52.95)	3.87 (3.46)	13.45 (13.23)	19.86 (20.17)	-	-	95	248 <sup>M</sup>	Creamish -white
2.	[Co(IN-DtczH-Sal) <sub>2</sub> ](Cl <sub>2</sub> ) <sub>2</sub> (C <sub>28</sub> H <sub>22</sub> N <sub>6</sub> O <sub>4</sub> S <sub>4</sub> Cl <sub>2</sub> Co) 764.45	43.84 (43.95)	2.69 (2.87)	10.89 (10.98)	16.65 (16.74)	7.59 (7.70)	9.13 (9.28)	90	230	Green
3.	[Co(IN-DtczH-Sal) <sub>2</sub> ](Br <sub>2</sub> ) <sub>2</sub> (C <sub>28</sub> H <sub>22</sub> N <sub>6</sub> O <sub>4</sub> S <sub>4</sub> Br <sub>2</sub> Co) 853.25	39.18 (39.38)	2.30 (2.58)	9.76 (9.84)	14.89 (15.00)	7.01 (6.90)	18.61 (18.73)	84	217	Dark brown
4.	[Co(IN-DtczH-Sal) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (C <sub>28</sub> H <sub>22</sub> N <sub>6</sub> O <sub>12</sub> S <sub>4</sub> Cl <sub>2</sub> Co) 892.45	37.43 (37.65)	2.31 (2.46)	9.30 (9.41)	14.14 (14.34)	6.99 (6.60)	-	88	286	Reddish brown
5.	[Co(IN-DtczH-Sal) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> (C <sub>28</sub> H <sub>22</sub> N <sub>8</sub> O <sub>10</sub> S <sub>4</sub> Co) 817.45	41.25 (41.10)	2.41 (2.69)	13.58 (13.70)	15.38 (15.66)	7.01 (7.21)	-	85	290	Dark brown
6.	[Co(IN-DtczH-Sal) <sub>2</sub> ](CH <sub>3</sub> COO) <sub>2</sub> (C <sub>32</sub> H <sub>28</sub> N <sub>6</sub> O <sub>8</sub> S <sub>4</sub> Co) 811.45	47.16 (47.32)	3.19 (3.45)	10.22 (10.35)	15.68 (15.77)	7.00 (7.26)	14.38 (14.54)	80	325	Brown
7.	[Co(IN-DtczH-Sal) <sub>2</sub> ](SO <sub>4</sub> ) <sub>2</sub> (C <sub>28</sub> H <sub>22</sub> N <sub>6</sub> O <sub>8</sub> S <sub>5</sub> Co) 789.45	42.41 (42.56)	2.59 (2.78)	10.42 (10.64)	20.12 (20.26)	7.54 (7.46)	12.02 (12.16)	83	220	Orange
8.	[Co(IN-DtczH-Sal) <sub>2</sub> ](C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> (C <sub>30</sub> H <sub>22</sub> N <sub>6</sub> O <sub>8</sub> S <sub>4</sub> Co) 781.45	46.23 (46.06)	2.61 (2.81)	10.62 (10.75)	16.16 (16.38)	7.67 (7.54)	11.13 (11.26)	78	240	Creamish -yellow
9.	[Co(IN-DtczH-Sal) <sub>2</sub> ](CO <sub>3</sub> ) <sub>2</sub> (C <sub>30</sub> H <sub>22</sub> N <sub>6</sub> O <sub>10</sub> S <sub>4</sub> Co) 753.45	47.64 (47.78)	2.81 (2.91)	11.02 (11.14)	16.79 (16.98)	7.77 (7.82)	7.88 (7.96)	75	300	Brown

**Table 2: Partial IR Spectral Absorptions (cm<sup>-1</sup>) of the Different Counter Anions of Cobalt Complexes of IN-DtczH-Sal Schiff Base**

Sr. No.	Compound	Band Assignments	Nature of Anion
1.	[Co(IN-DtczH-Sal) <sub>2</sub> ](SO <sub>4</sub> ) <sub>2</sub>	v <sub>3</sub> 1116 vs v <sub>4</sub> 619 s	Ionic
2.	[Co(IN-DtczH-Sal) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	v <sub>3</sub> 1088 vs v <sub>4</sub> 628 s	Ionic
3.	[Co(IN-DtczH-Sal) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	1384 vs 850-840 m	Ionic
4.	[Co(IN-DtczH-Sal) <sub>2</sub> ](C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	v(CO) modes 1675, 1355, 1288	Bridging
5.	[Co(IN-DtczH-Sal) <sub>2</sub> ](CO <sub>3</sub> ) <sub>2</sub>	v <sub>1</sub> (CO) 1384 s v <sub>3</sub> 771 m	Chelating bidentate
6.	[Co(IN-DtczH-Sal) <sub>2</sub> ](CH <sub>3</sub> COO) <sub>2</sub>	v <sub>a</sub> (OCO) 1568 vs v <sub>s</sub> (OCO) 1414 vs Δ 154	Ionic

## REFERENCES

- Ali, M.A., Mirza, A.H., Butcher, R.J. and Rahman, M., Trans. Met. Chem., 25 (2000) 430.
- Ali, M.A., Abu Bakar, H.J.H., Mirza, A.H., Smith, S.J., Gahan, L.R. and Bernhardt, P.V., Polyhedron, 27 (2008) 71.
- Chew, K-B., Tarafder, M.T.H., Crouse, K.A., Ali, A.M., Yamin, B.M. and Fun, H-K, Polyhedron, 23(8) (2004) 1385.
- Ali, M.A., Mirza, A.H., Butcher, R.J. and Crouse, K.A., Trans. Met. Chem., 31 (2006) 79.
- Rao, S.N., Kathale, N., Rao, N.N. and Munshi, K.N., Inorg. Chim. Acta, 360 (14) (2007) 4010.
- Rahman, M., Mridha, M.A. and Ali, M.A., Trans. Met. Chem., 19 (1994) 237.
- Livingstone, S.E., Quart. Rev., Chem. Soc., 19 (1965) 386.
- Kalia, S.B., Lumba, K., Kaushal, G. and Sharma, M., Ind. J. Chem., 46A (2007) 1233.
- Jagmohan, "Organic Spectroscopy- Principles and Applications", (2001).

10. Socrates, G., 'Infrared Characteristic Group Frequencies' John Wiley and Sons, Ltd., Great Britain (1980).
11. Ali, M.A., Mirza, A.H., Nazimuddin, M., Ahmed, R., Gahan, L.R. and Bernhardt, P.V., Polyhedron, 22 (2003) 1471.
12. Tarafder, M.T.H., Chew, K.-B., Crouse, K.A., Ali, A.M., Yamin, B.M. and Fun, H-K, Polyhedron, 21(27-28) (2002) 2683.
13. Makode, J.T. and Aswar, A.S., Ind.J.Chem., 43A (2004) 2120.
14. Ali, M.A., Nazimuddin, M., Shaha, R, Butcher, R.J. and Bryan, J.C., Polyhedron, 17(22) (1998) 3955.
15. Crouse, K.A., Chew, K.-B., Tarafder, M.T.H., Kasbollah, A., Ali, A.M., Yamin, B.M. and Fun, H-K., Polyhedron, 23(1) (2004) 161.
16. Ali, M.A., Mirza, A.H., Nazimuddin, M., Rahman, H. and Butcher, R.J., Trans. Met. Chem., 27(3) (2002) 268.
17. Ravoof, T.B.S.A., Crouse, K.A., Tahir, M.I.M., Cowley, A.R. and Ali, M.A., Polyhedron, 23 (2004) 2491.
18. Geary, W.J., Coord. Chem. Rev., 7 (1971) 81.
19. Nicholls, D, Comprehensive Inorg Chem (1973) 1053.
20. Ferguson, J., Wood, D.L. and Knox, K., J. Chem. Phys., 39 (1963) 881.
21. Lever, A.B.P., 'Inorganic Electronic Spectroscopy', Elsevier, New York (1984).