

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

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ABSTRACT

Some cobalt(II) complexes of acetylacetone Schiff base of isonicotinoyldithiocarbazic acid of the general formulae $[\text{Co}(\text{IN-DtczH-Acac})_2\text{X}_n]$ (IN-DtczH-Acac = acetylacetone Schiff base of isonicotinoyldithiocarbazic acid; X = Cl, Br, ClO_4 , NO_3 , CH_3COO for $n = 2$; X = SO_4 , C_2O_4 , CO_3 for $n = 1$) have been obtained and characterized by elemental analyses, infrared and electronic spectral and room temperature and variable temperature magnetic susceptibility measurements. All complexes exhibit ONS linkage of the ligand except the $\text{Co}(\text{IN-DtczH-Acac})_2\text{SO}_4$ complex in which the ligand IN-DtczH-Acac acts as a NS donor but the sulphate ion takes part in bonding resulting into bridged octahedral structure. The magnetic and electronic spectral studies suggest that all the complexes have high spin octahedral structures. $\text{Co}(\text{IN-DtczH-Acac})_2\text{SO}_4$ complex also exhibits intermolecular superexchange antiferromagnetic interactions in a sulphato bridged dimeric structure.

Keywords: Schiff base, IN-DtczH-Acac, infrared, electronic spectral, antiferromagnetic.

INTRODUCTION

Cobalt(II) being a borderline acid has the ability to form complexes with hard as well as soft bases. The Schiff bases derived from the condensation of various aldehydes and ketones with dithiocarbazic acids containing both hard nitrogen and soft sulphur donor atoms in their backbones, readily coordinate with a cobalt(II) yielding stable and intensely coloured metal complexes¹⁻⁴. Also, cobalt complexes exhibit varied stereochemistries (viz. tetrahedral, square planar, octahedral). Because of the small stability difference between octahedral and tetrahedral cobalt(II) complexes, there are several cases in which the two types with the same ligands are both known and may be in equilibrium. Also, cobalt(II) is rapidly oxidised to cobalt(III) in the presence of ligands with thiol groups⁵. Cobalt(II), thus offers a diversity in properties for its complexes to be studied. While the cobalt(II) complexes are reported with dithiocarbazic acid and dithiocarbazate ligands having $[\text{CoN}_2\text{S}_2]$, $[\text{CoO}_2\text{N}_2\text{S}_2]$, $[\text{CoN}_4\text{S}_2]$, $[\text{CoN}_4]$ and $[\text{CoS}_4]$, chromophores^{1-3,6-10}, the cobalt(III) complexes with $[\text{CoO}_2\text{N}_2\text{S}_2]$ ¹¹ chromophore are known to be formed as a result of oxidation of cobalt(II) to cobalt(III), when dithiocarbazate ester^{1,11,12} type of ligands are employed for bonding to the metal ion, though the reaction stoichiometry remains 1:2. These complexes exhibit tetrahedral, square planar, square pyramidal and octahedral stereochemistries^{1-4,6-9,13}. The present study was undertaken to probe the role of anion in deciding the type of stereochemistry as well as the spin state of cobalt(II) in its complexes with the IN-DtczH-Acac Schiff base ligand. While for such type of study in our earlier report with cobalt(II) complexes of IN-DtczH, cobalt(II) has been found to exist in different stereochemistries⁹.

MATERIALS AND METHODS

Cobalt(II) salts, isoniazid and CS_2 used were of analytical grade and used as such. Acetylacetone (sdfine, AR) was refluxed over P_2O_5 , distilled at 132 °C and finally stored in a P_2O_5 desiccator.

Preparation of IN-DtczH-Acac Schiff base: To a concentrated solution of isonicotinic acid hydrazide (1 g; 7.29 mmol) in ethanol (50 ml) was added with constant stirring 0.55 g, 7.29 mmol of carbon disulphide, when a light yellow liquid of the isonicotinoyldithiocarbazic acid was obtained. To this liquid kept at 40-45 °C was added drop-wise slightly less than the stoichiometric amount of acetylacetone (0.73 g; 7.29 mmol) with constant stirring. The resulting light yellow coloured solution was filtered and the filtrate was evaporated to give a white solid, Schiff base ligand. The ligand is obtained afresh (*in situ*) for the synthesis of its cobalt dithiocarbazate complexes because of stability reasons.

PREPARATION OF COMPLEXES

[Co(IN-DtczH-Acac)₂]_n (X = Cl, Br, NO₃, ClO₄, CH₃COO when n = 2 and X = SO₄ when n = 1):

To a continuously stirred ethanolic solution (50 ml) of IN-DtczH-Acac Schiff base (2.0 g; 6.77 mmol) prepared *in situ*, was added the solution of cobalt salt, CoX_n.xH₂O (0.81 g; 3.38 mmol for X = Cl; 1.11 g; 3.38 mmol for X = Br; 0.98 g; 3.38 mmol for X = NO₃ and 1.24 g; 3.38 mmol for X = ClO₄ and n = 2, x = 6; 0.84 g; 3.38 mmol for X = CH₃COO and n = 2, x = 4; 0.95 g; 3.38 mmol for X = SO₄ and n = 1, x = 7) in 30 ml ethanol (when X = Cl, Br, NO₃, ClO₄) or in 40 ml methanol (when X = CH₃COO and SO₄), 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 45-50 °C. Though the solid coloured product separates out immediately, yet the reaction mixture was stirred for another 2 hours to ensure the completion of the reaction. The solid product obtained was filtered through Whatman filter paper no. 541, washed with ethanol (when X = Cl, Br, NO₃, ClO₄) and with methanol (when X = CH₃COO and SO₄) and then with diethyl ether. It was then dried in air and finally the sample was dried by keeping it overnight in a calcium chloride desiccator.

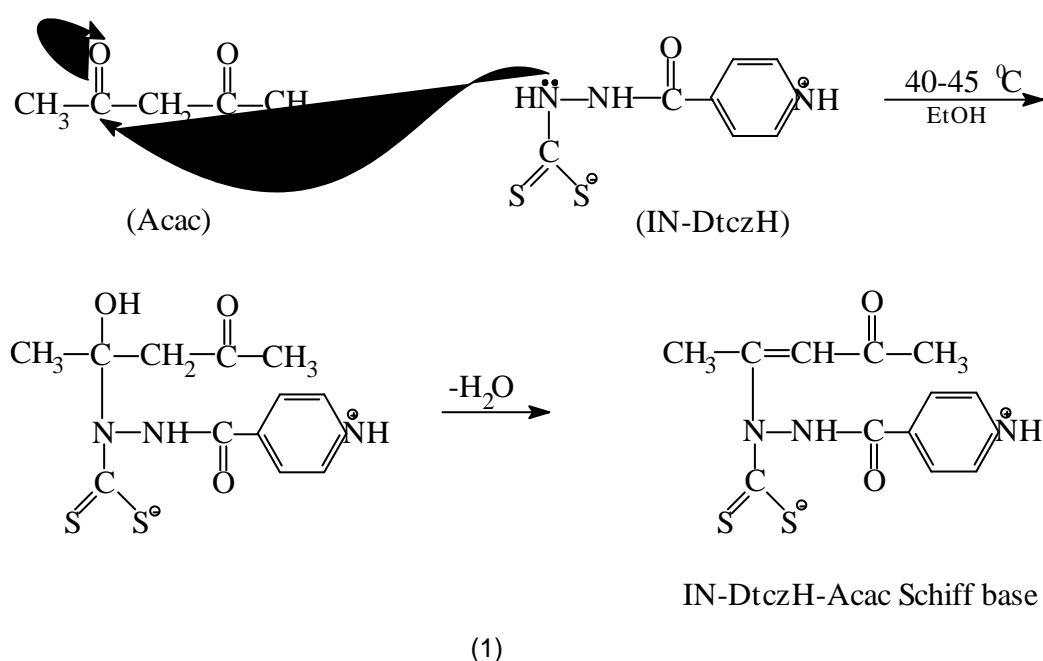
[Co(IN-DtczH-Acac)₂]_nX (X = C₂O₄, CO₃): Slightly less than the stoichiometric amount of solid cobalt salt CoX.xH₂O (0.62 g; 3.38 mmol for X = C₂O₄, x = 2; 0.40 g, 3.38 mmol for X = CO₃, x = 0) was added to a continuously stirred ethanolic solution (50 ml) of IN-DtczH-Acac Schiff base prepared *in situ* (2.0 g; 6.77 mmol). The contents of the reaction mixture were then continuously stirred and refluxed at 40-45 °C for about 72 hours. The solid product (brown) separated out immediately in case of CoCO₃. For the complex [Co(IN-DtczH-Acac)₂]₂C₂O₄, the light purple coloured solid separated near the end of the reaction. The product was filtered through Whatman filter paper no. 541, 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.

ELEMENTAL ANALYSES AND PHYSICAL MEASUREMENTS

Cobalt, chloride, bromide, oxalate, acetate and sulphur contents in the complexes were determined by the methods as reported earlier. Carbon, hydrogen and nitrogen analyses were performed on an Elementar Vario EL III Analyzer. IR and solution electronic spectral (DMSO) and magnetic susceptibility measurements and molar conductances (10⁻⁴ M solutions in DMSO at 25 ± 0.1 °C) were made according to earlier reported methods⁹.

RESULTS AND DISCUSSION

The Schiff base ligand, i.e. IN-DtczH-Acac has been obtained according to the reaction (1). The ligand was obtained afresh *in situ* for the synthesis of various cobalt complexes. The ligand obtained has Zwitterionic nature consequent upon its formation from the Zwitterionic IN-DtczH ligand.



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



X = Cl, Br, NO₃, ClO₄ for n = 2, x = 6

X = CH₃COO for n = 2, x = 4

X = SO₄ for n = 1, x = 7

X = C₂O₄ for n = 1, x = 2

X = CO₃ for n = 1, x = 0

Cobalt(II) complexes of IN-DtczH-Acac Schiff base are 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. They have some solubility in dimethylformamide and dimethylsulfoxide. All the complexes do not melt but decompose above 217-325 °C (Table 1).

INFRARED SPECTRAL STUDIES

Appearance of a new very strong band at 1444 cm⁻¹ ascribable due to C-N stretching vibrational mode and disappearance of the band due to ν(O-H) at 3005 cm⁻¹ in the IR spectrum of the IN-DtczH-Acac Schiff base ligand are indicative of the formation of Schiff base derivative of IN-DtczH with acetylacetone. The observation of this C-N vibrational mode at higher wave numbers in the free IN-DtczH-Acac ligand in comparison to the ν(C-N) (Amide III band) (1410 cm⁻¹) in IN-DtczH ligand can be attributed because of its conjugation with the C=C absorption of the acetylacetone part of the ligand. In the transition metal complexes of IN-DtczH-Acac this band disappears and mixes with the Amide III band and appears around 1419-1416 cm⁻¹, most probably because of its reduced conjugation with the

C=C bond, which now operates in the opposite direction with the C-C of the $\text{—CH—}\overset{\text{O}}{\parallel}\text{C—CH}_3$ group

because of the bonding of carbonyl oxygen of acetylacetone part of the IN-DtczH-Acac Schiff base ligand, to the cobalt(II). An increase¹⁴ as well as decrease¹⁵⁻¹⁸ in the ν(C-N) of Amide III band by about ~50 cm⁻¹ upon complexation has been reported by many authors by conjugation of the -C=N-C- group. Increase in the ν(C-N) IR frequency has been supported by X-ray crystallographic studies from the strengthening of the C-N bond upon complexation by 0.042 Å in the nickel(II) and copper(II) complexes with S-methyl-□-N-(4-nitrobenzal)methylenedithiocarbamate¹⁴. Non observation of the band due to ν(SH) at 2570 cm⁻¹ in the IN-DtczH-Acac Schiff base ligand, further indicates that the ligand remains in its thione form and not the thiol form^{6,19-20}. The appearance of the ν(N-H) mode at higher wave numbers 3600-3000 cm⁻¹ (Table 2) than the usually observed range further indicates that the IN-DtczH-Acac ligand also exists as a Zwitterion in the free state as well as in its transition metal complexes. This further rules out the possibility of the existence of the Schiff base in the thione form.

For the amide group (-CONH-) of the heteroaroyl dithiocarbazic acid part of the IN-DtczH-Acac ligand, a single very strong and broad band at 1624 cm⁻¹ has been observed. This group shows its absorption at 1653 cm⁻¹ for the free IN-DtczH ligand. Observation of a single very strong and broad band at 1624 cm⁻¹ in the IN-DtczH-Acac Schiff base ligand infers the overlapping of the two carbonyl stretching absorptions due to acetylacetone and heteroaroyl group of IN-DtczH of the IN-DtczH-Acac Schiff base derivative. The downfield shift of the Amide I band, may arise because of the conjugation of the C=C bond upon formation of a new C-N bond of the Schiff base. All the cobalt complexes of this Schiff base exhibit a very strong doublet for this group in the range 1657-1653 cm⁻¹ and 1614-1608 cm⁻¹. The former range corresponds to the absorption due to Amide I band of IN-DtczH part of the ligand, wherein no shift in band frequency has been observed when compared with free IN-DtczH ligand and is indicative of the fact that carbonyl group of the amide function is not taking part in bond formation with the central metal ion. The latter band at 1614-1608 cm⁻¹ exhibiting a down field shift of about 10-16 cm⁻¹ in comparison to the carbonyl stretching frequency of the acetylacetone part of the ligand, suggests the bonding of this carbonyl group with cobalt in all of its cobalt complexes except in Co(IN-DtczH-Acac)₂SO₄ complex, wherein it remains unshifted. The ν(C-N) of -CONH- (Amide III band) appears at 1406 cm⁻¹ in free IN-

DtczH-Acac ligand while this band exhibits an upfield shift of $10\text{--}13\text{ cm}^{-1}$ in all the complexes and appears in the range $1419\text{--}1416\text{ cm}^{-1}$, indicating coordination of the amide nitrogen to the metal ion with concomitant strengthening of the C-N bond of the amide group through strong conjugation of the —C=N—N=C— grouping. Such a strong conjugation in this group is also evident from the X-ray diffraction studies on copper(II) complexes of di-2-pyridylketone Schiff base of S-methyldithiocarbamate²¹.

The spectra of all cobalt - IN-DtczH-Acac complexes exhibit strong absorption near $1025\text{--}1017\text{ cm}^{-1}$ either being split up into two bands or has well defined shoulders²¹⁻²³. This further supports the postulate of unidentate sulphur coordination associated with the ONS bonded structure.

Presence of infrared absorption bands for the different mononegative oxo anions, viz. acetate, perchlorate and nitrate in these complexes reveals their non coordinating nature (Table 3). The dinegative anions, viz. oxalate and carbonate, though exhibit ionic behaviour (Table 3) yet their charge neutralization occurs through intermolecular electrostatic as well as hydrogen bonding interactions (Fig 3) The sulphate group in the complex $\text{Co(IN-DtczH-Acac)}_2\text{SO}_4$ exhibits bands at $991\text{ m}(\nu_1)$; $465\text{ m}(\nu_2)$; 1058 s , $1148\text{ s}(\nu_3)$ and 650 s , $618\text{ s}(\nu_4)$ corresponding to its bridging bidentate nature resulting into $[\text{CoO}_2\text{N}_2\text{S}_2]$ chromophore.

MOLAR CONDUCTANCE STUDIES

The molar conductance values of 10^{-4} M DMSO solutions of the complexes of the general formula $[\text{Co(IN-DtczH-Acac)}_2]\text{X}_n$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4, \text{CH}_3\text{COO}$ for $n = 2$) lie in the range $168\text{--}175\text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ (Table 2) corresponding to 1:2 electrolytic behaviour²⁴. While for the complexes with $\text{X} = \text{C}_2\text{O}_4$ and CO_3 for $n = 1$, the molar conductance values lie in the range $68\text{--}85\text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ (Table 2) corresponding to 1:1 electrolytic behaviour. The $\text{Co(IN-DtczH-Acac)}_2\text{SO}_4$ complex is non-electrolytic in nature.

MAGNETIC SUSCEPTIBILITY STUDIES

The room temperature magnetic moment values for the six coordinate cobalt(II), d^7 complexes of the present study range from $4.69\text{--}5.38\text{ B.M.}$ and suggest the possibility of either high-spin octahedral or tetrahedral structures for these complexes²⁵. The variable temperature ($299\text{--}80\text{ K}$) magnetic susceptibility data indicate that the magnetic moment values decrease as the temperature is lowered (Figure 1).

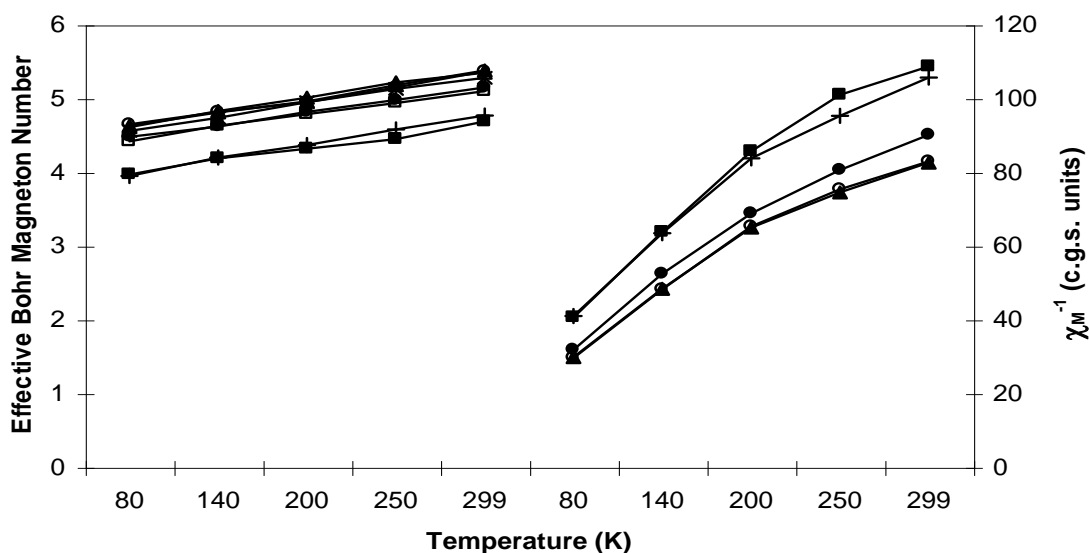


Fig. 1: Variation of Effective Bohr Magnetron Numbers and χ_M^{-1} of $[\text{Co(IN-DtczH-Acac)}_2]\text{Cl}_2$ (—x—), $[\text{Co(IN-DtczH-Acac)}_2]\text{Br}_2$ ($\text{—}\Delta\text{—}$), $[\text{Co(IN-DtczH-Acac)}_2](\text{ClO}_4)_2$ ($\text{—}\square\text{—}$), $[\text{Co(IN-DtczH-Acac)}_2](\text{NO}_3)_2$ ($\text{—}\bullet\text{—}$), $[\text{Co(IN-DtczH-Acac)}_2](\text{CH}_3\text{COO})_2$ ($\text{—}\blacksquare\text{—}$), $[\text{Co(IN-DtczH-Acac)}_2]\text{C}_2\text{O}_4$ ($\text{—}+\text{—}$), $\text{Co(IN-DtczH-Acac)}_2\text{SO}_4$ ($\text{—}\circ\text{—}$), $[\text{Co(IN-DtczH-Acac)}_2]\text{CO}_3$ ($\text{—}\blacktriangle\text{—}$) with Temperature

These complexes though were prepared in 1:2 metal to ligand stoichiometric ratio thus suggesting four coordination number with planar or tetrahedral stereochemistry around the central metal ion. But, as discussed earlier, infrared spectral study reveals that the Schiff base ligand IN-DtczH-Acac has been found to act as a tridentate ONS donor in all its cobalt(II) complexes irrespective of the nature (uninegative or dinegative) of the counter anion except in the $\text{Co}(\text{IN-DtczH-Acac})_2\text{SO}_4$ complex where it behaves as a bidentate NS donor. In the complex $\text{Co}(\text{IN-DtczH-Acac})_2\text{SO}_4$, 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. sulphate resulting into bridged octahedral structure. On the basis of the observed range of μ_{eff} values (Table 4) and their temperature dependent behaviour supported by six coordination from IR spectral study for all the complexes, high spin octahedral structures have been proposed.

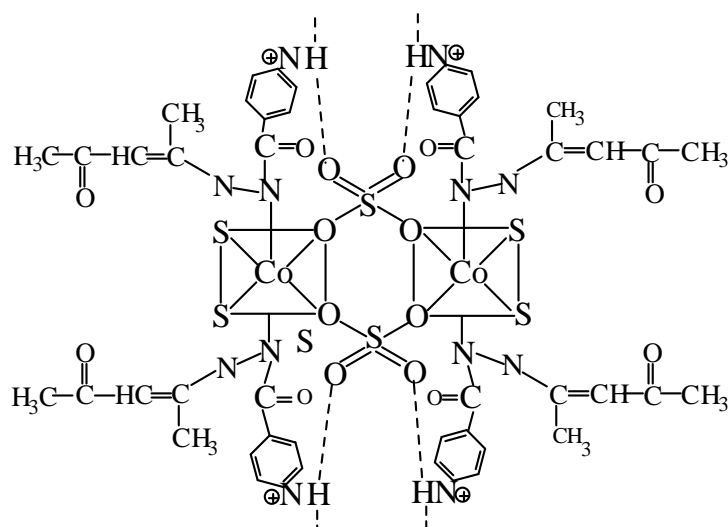


Fig. 2: Proposed structure for the $\text{Co}(\text{IN-DtczH-Acac})_2\text{SO}_4$ complex

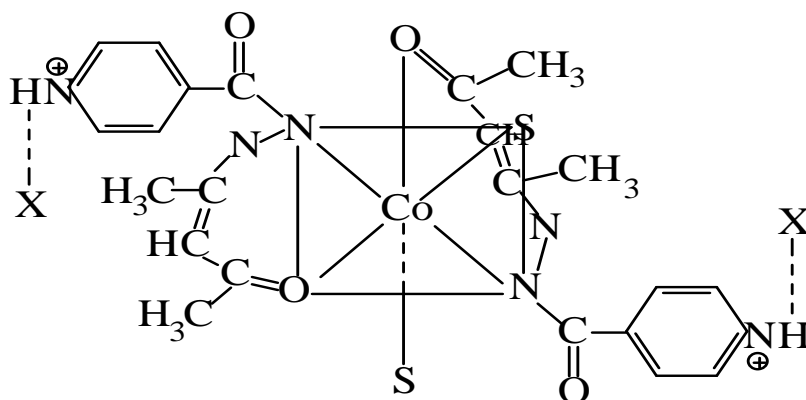


Fig. 3: Proposed structure for the $[\text{Co}(\text{IN-DtczH-Acac})_2]\text{X}_n$ Complexes ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4, \text{CH}_3\text{COO}, \text{C}_2\text{O}_4, \text{CO}_3$)

ELECTRONIC ABSORPTION SPECTRAL STUDIES

The DMSO solution electronic absorption spectra of all the cobalt(II) dithiocarbazate complexes exhibit two bands around 9,750-11,495 cm^{-1} in the near infrared region and around 20,000-26,600 cm^{-1} in the visible region (Table 4). These have been assigned to the $\nu_1[{}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)]$ and $\nu_3[{}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)]$ transitions respectively. The band in the visible region has a shoulder around 14,285-17,590 cm^{-1} on low-energy side assigned to the $\nu_2[{}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)]$ transition and it shows a sign of splitting. In the $[\text{Co}(\text{IN-DtczH-Acac})_2]X_n$ ($X = \text{CH}_3\text{COO}$ when $n = 2$; $X = \text{C}_2\text{O}_4$ when $n = 1$) complexes, intense bands are observed on the low energy side of the band in the visible region which are assigned to spin forbidden transitions originating in 2G . These bands are of reasonable intensity probably because of exchange processes occurring in the octahedral polymeric species, the octahedral being bridged by the respective anions. The observation of the sign of splitting for the shoulder around 14,285-17,590 cm^{-1} can be attributed to the spin-orbit coupling, vibrational broadening, low symmetry components to the ligand field or transitions to doublet states^{25,26}. The presence of low symmetry ligand field component in the complexes having uninegative anions can be attributed to the inequivalent nature of the ligand donor atoms.

The ligand field experienced for the high spin octahedral cobalt(II) in its dithiocarbazate complexes has been calculated in terms of the ligand field parameter, $10Dq$. The range of ligand field parameters, viz. $10Dq$, B and β' values and the electronic spectral band assignments give an acceptable account of the spectra^{25,26}, which no other assignment of the bands provides, and it must be regarded as essentially correct. The range of B and $10Dq$ values match with those reported earlier.

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 ₁₄ H ₁₁ N ₃ O ₂ S ₂) 317.28	52.49 (52.95)	3.87 (3.46)	13.45 (13.23)	19.86 (20.17)	-	-	95	248 ^m	Creamish -white
2.	[Co(IN-DtczH-Sal) ₂]Cl ₂ (C ₂₈ H ₂₂ N ₆ O ₄ S ₄ Cl ₂ 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) ₂]Br ₂ (C ₂₈ H ₂₂ N ₆ O ₄ S ₄ Br ₂ 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) ₂](ClO ₄) ₂ (C ₂₈ H ₂₂ N ₆ O ₁₂ S ₄ Cl ₂ 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) ₂](NO ₃) ₂ (C ₂₈ H ₂₂ N ₈ O ₁₀ S ₄ 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) ₂](CH ₃ COO) ₂ (C ₃₂ H ₂₈ N ₆ O ₈ S ₄ 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) ₂]SO ₄ (C ₂₈ H ₂₂ N ₆ O ₈ S ₅ 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) ₂]C ₂ O ₄ (C ₃₀ H ₂₂ N ₆ O ₈ S ₄ 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) ₂]CO ₃ (C ₃₀ H ₂₂ N ₆ O ₁₀ S ₄ 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: Some Coordinatively Diagnostic Features of Infrared Spectra (cm⁻¹) and Molar Conductance Values, Λ_m (ohm⁻¹cm²mol⁻¹) of IN-DtczH-Sal Schiff Base and its Cobalt(II) Complexes

Sr. No.	Compound	$\nu(\text{N-H}) / \nu(\text{O-H})$	Amide I $\nu(\text{C=O})$	Amide III $\nu(\text{C-N})$	Azomethine $\nu(\text{N-N})$	$\nu_a(\text{CS})$	$\nu(\text{M-S})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	Λ_m
1.	IN-DtczH-Sal	3200-3100 b,s	1652 vs	1408 s	1064 s	1032,999 s	-	-	-	-
2.	[Co(IN-DtczH-Sal) ₂]Cl ₂	3600-3200 b,s	1656 vs	1443 s	1065 s	1020,995 s	360 m	340 m	-	178
3.	[Co(IN-DtczH-Sal) ₂]Br ₂	3600-3000 b,s	1656 vs	1443 s	1064 s	1020,994 s	325 m 319 m	332 m 326 m	-	160
4.	[Co(IN-DtczH-Sal) ₂](ClO ₄) ₂	3550-3000 b,s	1659 vs	1443 s	1065 s	1015,990 s	355 m 348 m	325 m 333 m	-	165
5.	[Co(IN-DtczH-Sal) ₂](NO ₃) ₂	3550-3350 b,s	1657 vs	1443 s	1060 s	1030,998 s	390 m	320 m	-	165
6.	[Co(IN-DtczH-Sal) ₂](CH ₃ COO) ₂	3550-3250 b,s	1653 vs	1444 s	1060 s	1030,995 s	345 m	335 m	-	170
7.	[Co(IN-DtczH-Sal) ₂]SO ₄	3600-3000 b,s	1655 vs	1439 s	1068 s	1034,999 s	380 m 372 m	348 m 340 m	-	80
8.	[Co(IN-DtczH-Sal) ₂]C ₂ O ₄	3550-3250 b,s	1657 vs	1442 s	1066 s	1025,997 s	375 m 368 m	327 m 320 m	-	75
9.	Co(IN-DtczH-Sal) ₂ CO ₃	3570-3250 b,s	1658 vs	1439 s	1067 s	1030,999 s	378 m	340 m	440 m	7

Table 3: Partial IR Spectral Absorptions (cm⁻¹) 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) ₂ SO ₄]	ν_3 1116 vs ν_4 619 s	Ionic
2.	[Co(IN-DtczH-Sal) ₂](ClO ₄) ₂	ν_3 1088 vs ν_4 628 s	Ionic
3.	[Co(IN-DtczH-Sal) ₂](NO ₃) ₂	1384 vs 850-840 m	Ionic
4.	[Co(IN-DtczH-Sal) ₂]C ₂ O ₄	ν (CO) modes 1675, 1355, 1288	Bridging
5.	Co(IN-DtczH-Sal) ₂ CO ₃	ν_1 (CO) 1384 s ν_3 771 m	Chelating bidentate
6.	[Co(IN-DtczH-Sal) ₂](CH ₃ COO) ₂	ν_a (OCO) 1568 vs ν_s (OCO)1414 vs Δ 154	Ionic

Table 4: Electronic Absorption Spectra (cm⁻¹) and μ_{eff} Values of High Spin Octahedral Cobalt(II) Isonicotinoyldithiocar-bazate Complexes

Sr. No.	Compound	Binding Mode Of Ligand	Band Assignments			μ_{eff} (B.M.)
			$\nu_3 [{}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)]$	$\nu_2 [{}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)]$	$\nu_1 [{}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)]$	
1.	Co(IN-DtczH) ₂ SO ₄	NS/SO ₄ bridging	20,000	15,400	9,500	4.70
2.	[Co(IN-DtczH) ₂]C ₂ O ₄	ONS	19,600	14,705	10,810	5.05
3.	[Co(IN-DtczH-Acac) ₂]Cl ₂ *	ONS	24,270	16,850, 15,150	11,260	5.28
4.	[Co(IN-DtczH-Acac) ₂]Br ₂	ONS	24,400	-	11,210	5.35
5.	[Co(IN-DtczH-Acac) ₂](ClO ₄) ₂	ONS	24,690	14,285	11,430	5.10
6.	[Co(IN-DtczH-Acac) ₂](NO ₃) ₂	ONS	24,650	17,590	11,235	5.15
7.	[Co(IN-DtczH-Acac) ₂](CH ₃ COO) ₂	ONS	26,600	17,545	11,175	4.69
8.	[Co(IN-DtczH-Acac) ₂]C ₂ O ₄	ONS	23,000	17094, 14492	11,170	4.77
9.	Co(IN-DtczH-Acac) ₂ SO ₄	NS/ SO ₄ bridging	24,390	14,300	11,495	5.37
10.	[Co(IN-DtczH-Acac) ₂]CO ₃	ONS	20,000	-	9,750	5.38
11.	Co(IN-DtczH-Sal) ₂ CO ₃	NS/ CO ₃ binding	23,200	14,925	11,200	5.36
12.	[Co ₂ (IN-DtczH)(O ₂) ₂ CO ₃] ₂ .CoO	ONS	19,230	14,285	9,500**	7.50

* IN-DtczH-Acac intraligand absorption: 37,000 cm⁻¹** ${}^5E_g \leftarrow {}^5T_{2g}$ and ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ **REFERENCES**

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