

## Metal Complexes with Dicyclohexanone/Disalicylidene Carbohydrazone

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Metal(II) complexes of the type  $[M_2(DCHC)_2(H_2O)_4]X_2$  and  $[M_2(DSC)_2]$  where  $M = Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}$  and  $Hg^{2+}$ , DCHC = dicyclohexanone carbohydrazone and DSC = disalicylidene carbohydrazone and  $X = Cl^-, Br^-$  and  $NO_3^-$  have been isolated in neutral medium. All the complexes except of  $Zn^{2+}, Cd^{2+}$  and  $Hg^{2+}$  are paramagnetic. The complexes with DCHC have octahedral stereochemistry and complexes with that of DSC except copper have tetrahedral stereochemistry around the metal ions.

### INTRODUCTION

A large number of transition metal complexes with ligands containing nitrogen donor atoms such as hydrazine and substituted hydrazine is of special interest because of the variety of the ways in which these species can be bonded to the metal ions<sup>1,2</sup>. In continuation to our study on the dimeric metal complexes with Schiff bases as ligand<sup>3</sup>, we report here some dimeric metal complexes with Schiff bases obtained on the condensation of cyclohexanone/salicylaldehyde with carbohydrazone.

### EXPERIMENTAL

All the chemicals used were of E. Merck/B.D.H. AnalaR grade or extra pure quality.

*Preparation of the ligand:* Carbohydrazone was prepared by refluxing diethyl carbonate with hydrazine. The Schiff bases were prepared by condensation of cyclohexanone/salicylaldehyde with carbohydrazone in 2:1 molar ratio, by refluxing in methanol in the presence of a few drops of piperidine. After refluxing for 1 h the excess of the solvent was removed under reduced pressure. The solids thus obtained were filtered off and crystallised with methanol and analysed. The analytical data are recorded in Table-1.

TABLE-1  
ANALYTICAL DATA OF THE LIGANDS

Complexes	Colour	% Found (Calcd.)		
		C	H	N
$C_{13}H_{22}N_4O$	DCHC(Yellow)	62.30 (62.40)	8.78 (8.80)	22.22 (22.4)
$C_{15}H_{14}N_4O_3$	DSC(White)	60.32 (60.40)	4.61 (4.69)	18.77 (18.79)

DCHC—Dicyclohexanone Carbohydrazone, DSC—Disalicylidene Carbohydrazone.

### Synthesis of the complexes

The methanolic solution of the appropriate metal salt and ligand in the molar ratio 1 : 1 was refluxed on a water bath for 1 h. Then moderately hot solution was vigorously shaken and finally cooled. A precipitate was slowly formed which was aged by digesting on the water bath for 1 h. It was then filtered, washed with methanol several times and dried in vacuum for 24 h and then analysed. The purity of the isolated complexes were established by standard methods<sup>5-8</sup>. The analytical results of the complexes are recorded in Table-2.

TABLE-2  
ANALYTICAL DATA OF LIGANDS AND THEIR METAL COMPLEXES

Complexes/colour	m.p. (°C)	Yield %	% Found (Calcd.)		
			M	N	Halogen
[Cu <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> (green)	250	84	16.48 (16.53)	14.41 (14.58)	9.21 (9.24)
[Cu <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Br <sub>2</sub> (yellowish green)	250	86	14.36 (14.82)	12.91 (13.06)	18.06 (18.67)
[Cu <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> (green)	250	83	15.41 (15.47)	16.87 (17.07)	—
[Co <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> (blue)	250	82	14.48 (15.54)	14.72 (14.76)	8.97 (9.36)
[Co <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Br <sub>2</sub> (blue)	250	80	13.59 (13.91)	13.12 (13.21)	18.51 (18.87)
[Co <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> (blue)	250	85	14.41 (14.53)	17.04 (17.24)	—
[Ni <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> (yellow)	250	87	15.28 (15.54)	14.77 (14.76)	9.21 (9.36)
[Ni <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Br <sub>2</sub> (greenish yellow)	250	84	13.11 (13.91)	13.18 (13.21)	18.67 (18.87)
[Ni <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> (blue)	250	89	14.21 (14.53)	17.12 (17.24)	—
[Zn <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> (white)	250	81	16.49 (16.86)	14.50 (14.53)	9.02 (9.21)
[Zn <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Br <sub>2</sub> (white)	250	85	14.69 (15.11)	12.85 (13.02)	18.56 (18.60)
[Zn <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> (white)	250	82	15.42 (15.77)	16.75 (16.99)	—
[Cd <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> (white)	250	87	25.83 (25.89)	12.90 (12.94)	8.17 (8.21)
[Cd <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Br <sub>2</sub> (white)	250	81	23.42 (23.48)	11.32 (11.74)	16.51 (16.77)

Complexes/colour	m.p. (°C)	Yield %	% Found (Calcd.)		
			M	N	Halogen
[Cd <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> (white)	250	84	24.44 (24.40)	14.99 (15.25)	—
[Hg <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>2</sub> (orange)	250	76	37.89 (38.54)	10.75 (10.73)	6.54 (6.80)
[Hg <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]Br <sub>2</sub> (orange)	250	78	35.02 (35.51)	9.65 (9.89)	13.87 (14.13)
[Hg <sub>2</sub> (DCHC) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> (orange)	250	76	36.06 (36.67)	12.72 (12.77)	—
[Cu <sub>2</sub> (DSC) <sub>2</sub> ] (dirty green)	250	86	17.73 (17.56)	15.00 (15.49)	—
[Co <sub>2</sub> (DSC) <sub>2</sub> ] (green)	250	89	16.12 (16.50)	15.60 (15.69)	—
[Ni <sub>2</sub> (DSC) <sub>2</sub> ] (yellowish green)	250	87	16.49 (16.46)	15.46 (15.70)	—
[Zn <sub>2</sub> (DSC) <sub>2</sub> ] (yellowish white)	250	85	17.69 (17.99)	15.40 (15.41)	—
[Cd <sub>2</sub> (DSC) <sub>2</sub> ] (white)	250	84	27.40 (27.38)	13.66 (13.65)	—
[Hg <sub>2</sub> (DSC) <sub>2</sub> ] (yellow)	250	81	39.88 (40.23)	11.11 (11.23)	—

## RESULTS AND DISCUSSION

All the complexes isolated in the solid state were insoluble in water as well as in common organic solvents such as ethanol, acetone and dioxane. The complexes are slightly soluble in DMF and DMSO. The freshly prepared solution of DSC complexes are non-electrolytic nature but the complexes of DCHC are electrolytic in DMSO.

### Infrared spectra

The carbohydrazides possess a ketoamide group (—CONH) and an—NH<sub>2</sub> group of hydrazine moiety. Thus in the higher frequency region the IR spectrum displays a strong and very broad band between 3340–3000 cm<sup>-1</sup> attributed to  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$  vibration of NH and NH<sub>2</sub> groups<sup>10-12</sup>. The broadness of the band indicates hydrogen bonding in the carbohydrazide molecule<sup>13, 14</sup>. But in the ligand dicyclohexanone carbohydrazone, this band is found to be absent instead a sharp and strong band appears at *ca.* 3400 cm<sup>-1</sup> which is characteristic of  $\nu(\text{N—H})$  for secondary amides indicating the absence of  $\nu(\text{NH}_2)$  vibration which generally appears comparatively at lower frequency region.

In the metal complexes, this band further broadens suggesting non-involvement of the secondary amide—NH group in coordination and presence of

coordinated water molecule. The broadening of the band is probably due to strong hydrogen-bonding. This observation is supported by the conspicuous absence of an infrared band in the spectrum of the ligand which is observed in case of the carbohydrazide molecule at *ca.* 1655  $\text{cm}^{-1}$  and is assigned to a combination mode due to  $\delta(\text{NH}_2)$  and  $\nu(\text{CO})$  vibration of a secondary amide group. Instead, a strong and sharp band appears at *ca.* 1680  $\text{cm}^{-1}$  in the infrared spectrum of DCHC characteristic of  $\nu(\text{C}=\text{O})$  vibration. However, in the infrared spectra of the complexes this band undergoes a hypsochromic shift by 10–15  $\text{cm}^{-1}$  indicating the coordination of the carbonyl group to the metal ion<sup>15</sup>. The  $\nu(\text{C}=\text{N})$  vibration which appears at 1600  $\text{cm}^{-1}$  in the infrared spectrum of carbohydrazide is observed at 1610  $\text{cm}^{-1}$  as a medium broad band in the spectrum of the ligand. This band suffers bathochromic shift in the infrared spectra of all the metal complexes suggesting the involvement of the azomethine nitrogen in coordination. This observation is substantiated by shifting of  $\nu(\text{N}-\text{N})$  vibration from 1130  $\text{cm}^{-1}$  to 1120  $\text{cm}^{-1}$  in the spectra of all the metal complexes. In the nitro complexes the absence of bands around 1390 and 1310  $\text{cm}^{-1}$  suggest the non-coordination of the nitrate ion to the central metal ion<sup>16</sup>. A few additional bands at *ca.* 430 and 410  $\text{cm}^{-1}$  are observed in the lower frequency region of the spectra. The former may be tentatively assigned to  $\nu(\text{M}-\text{N})$ , while latter is assigned to  $\nu(\text{M}-\text{O})$ <sup>17, 18</sup>.

In DSC complexes the infrared spectrum of carbohydrazide possess a strong and broad band at 3340–3000  $\text{cm}^{-1}$  which is reasonably assigned to a combination of  $\nu\text{NH}$  and  $\nu\text{NH}_2$  vibration<sup>11, 12</sup>. This band is found to be absent in the spectrum of ligand (DSC) as well as of the metal complexes. Instead a strong and broad band is observed in the infrared spectrum of the ligand around 3420  $\text{cm}^{-1}$  which is perhaps a split component of the cumulative band due to  $\nu\text{NH}$  and  $\nu\text{NH}_2$  and is characteristic of a  $\nu\text{NH}-$  (secondary amide) vibration<sup>19</sup>. This band does not undergo any shift in the spectra of the complexes suggesting non involvement of the nitrogen of the  $-\text{CONH}$  group in coordination.

A band of medium intensity observed in the spectrum of ligand (DSC) at *ca.* 2950  $\text{cm}^{-1}$  may be due to (OH) mode intramolecularly hydrogen bounded phenolic OH group<sup>20, 21</sup>. The presence of OH group is also indicated by the appearance of another band of medium intensity in the infrared spectrum of ligand at 1190  $\text{cm}^{-1}$  which is assigned to wagging and rocking mode of  $-\text{OH}$  vibrations<sup>22</sup>. These bands are absent in the spectra of the complexes suggesting the deprotonation of the phenolic OH group on complex formation. In the infrared spectrum of the ligand a band of medium intensity observed at 1470  $\text{cm}^{-1}$  is assigned to phenolic  $\nu(\text{C}-\text{O})$  vibration which undergoes a hypsochromic shift in the infrared spectra of the complexes. This observation suggests the deprotonation of phenolic OH group and coordination of the phenolic oxygen atom to the central metal ion<sup>23</sup>.

Carbohydrazide displays a number of bands in its infrared spectrum at 1655, 1600, 1033 and 912  $\text{cm}^{-1}$  which are assigned to ( $\nu\text{NH}_2 + \nu\text{C}=\text{O}$ ),  $\nu(\text{C}=\text{N})$ ,  $\delta\text{NH}_2$  (wagging) and  $\delta\text{NH}_2$  (rocking) modes of vibration respectively<sup>24, 25</sup>. These bands are found to be absent in the infrared spectra of the ligand as well as in those of complexes.

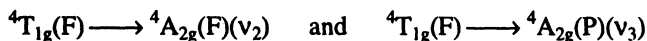
However, the infrared spectrum of ligand shows a strong band at *ca.* 1680  $\text{cm}^{-1}$  characteristic of secondary amide  $\nu(\text{C}=\text{O})$  vibration which does not suffer any change on complexation. Similarly  $\delta(\text{NH})$ ,  $\nu(\text{C}-\text{N})$  and  $\delta(\text{NH})$  present in the spectra of the carbohydrazide and the ligand (DSC) at 1520, 1200 and 750  $\text{cm}^{-1}$  respectively remain practically unchanged in the spectra of the complexes suggesting non-participation of the oxygen of the amide carbonyl group ( $\text{C}=\text{O}$ ) and nitrogen of the secondary amide group ( $-\text{CONH}$ ) in coordination. The bathochromic shift of strong and sharp bands observed in the infrared spectrum of the ligand at *ca.* 1640 and 1130  $\text{cm}^{-1}$  characteristic of  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{N}-\text{N})$  vibrations respectively in an unambiguous evidence for coordination through azomethine nitrogen atoms<sup>26, 27</sup>. Further in the region 500–400  $\text{cm}^{-1}$  some new bands are observed at *ca.* 430 and 410  $\text{cm}^{-1}$  in the spectra of the metal complexes which are assigned to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  stretching vibration respectively<sup>17, 18</sup>.

From the forging observation it is obvious that the ligand molecule behaves as a tetradentate dimeric species. Considering the transplanarity of the ligand molecule, it cannot coordinate to the same metal ion. A polymeric structure will satisfy our observation.

### Electronic spectra and magnetic moment of the complexes

The electronic spectra of the ligand was recorded in dioxane and the spectral data is recorded in Table-3. The ligand DCHC show two electronic absorption band near *ca.* 35,710 and 33,330  $\text{cm}^{-1}$ . The intensity and width of the absorption bands lead us to suggest that these bands most probably arised due to  $\pi \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions<sup>28</sup> respectively. The ligand DSC also shows two bands near 35,090 and 27,800, these bands most probably arised due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition<sup>28</sup> respectively.

The electronic spectra, magnetic moment value and ligand field parameters for the complexes are presented in Table-3. The  $\text{Co}^{2+}$  complexes show a band system in the region 12,000–15,000 and 16,000–20,000  $\text{cm}^{-1}$  assigned to



transitions respectively which can be unambiguously interpreted to arise due to ligand field transitions of the octahedral component of  $\text{Co}(\text{II})$  complexes. The magnetic moment value of  $\text{Co}(\text{II})$  complexes were obtained in between 5.01–5.21 BM expected for high spin octahedral  $\text{Co}(\text{II})$  ion. The position of the electronic absorption band and the values of ligand field parameters calculated from  $\nu_2$  and  $\nu_3$  transition indicates the presence of octahedral geometry in case of  $\text{Co}(\text{II})$  complexes which is supported by magnetic moment value<sup>29</sup>.

The  $\text{Ni}(\text{II})$  complexes investigated in the present study exhibit simple spectra involving three spin allowed transitions to the  ${}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{T}_{1g}(\text{P})$  levels assuming octahedral ligand field around the metal ion, the ground term being  ${}^3\text{A}_{2g}(\text{F})$ . These occurs in the region 7000–13000 ( $\nu_1$ ), 11000–20000 ( $\nu_2$ ) and 19000–27000 ( $\nu_3$ ) corresponding to the transition  ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{2g}(\text{F})(\nu_1)$ ,  ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{A}_{1g}(\text{F})(\nu_2)$  and  ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$  respectively. The ligand field parametes are calculated by adopting octahedral model. The value compared

TABLE-3  
ELECTRONIC SPECTRAL DATA, MAGNETIC MOMENTS AT ROOM TEMPERATURE AND LIGAND FIELD PARAMETERS OF Co(II) AND Ni(II) COMPLEXES

Compound	$\mu_{\text{eff}}$ (B.M.)	Electronic spectral bands in $\text{cm}^{-1}$	Assignments	Ligand field parameters ( $\text{cm}^{-1}$ )						
				$D_q$	B	C	$F_2$	$F_4$	$\beta$	
DCHC	—	35,710 33,330	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	—	—	—	—	—	—	—
$[\text{Co}_2(\text{DCHO})_2(\text{H}_2\text{O})_4]\text{Cl}_2$	5.21	12,350 16,600	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{1g}(\text{P})(\nu_3)$	698	775	3592	1288	103.0	0.80	
$[\text{Co}_2(\text{DCHO})_2(\text{H}_2\text{O})_4]\text{Br}_2$	5.18	16,000 17,860	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{1g}(\text{P})(\nu_3)$	793	760	3522	1265	101.0	0.78	
$[\text{Co}_2(\text{DCHO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$	5.01	15,850 17,400	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{1g}(\text{P})(\nu_3)$	843	740	3492	1230	99.5	0.76	
$[\text{Ni}_2(\text{DCHO})_2(\text{H}_2\text{O})_4]\text{Cl}_2$	2.89	11,630 19,610	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$	744	676	3140	1130	91.0	0.66	
$[\text{Ni}_2(\text{DCHO})_2(\text{H}_2\text{O})_4]\text{Br}_2$	2.93	11,750 20,000	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$	760	690	3218	1140	93.0	0.69	
$[\text{Ni}_2(\text{DCHO})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$	2.97	11,760 19,420	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$	783	710	3250	1137	94.0	0.70	
DSC	—	35,090 27,800	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	—	—	—	—	—	—	—
$[\text{Co}_2(\text{DSC})_2]$	3.82	8,200 16,600	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})(\nu_2)$ ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$	522	652	2886	1065	82.5	0.71	
$[\text{Ni}_2(\text{DSC})_2]$	4.40	11,600 17,400	${}^3\text{T}_{1g}(\text{P}) \rightarrow {}^3\text{A}_{2g}(\text{F})(\nu_2)$ ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$	636	848	3748	1383	107.1	0.81	

to that of free Ni(II) ion ( $1030\text{ cm}^{-1}$ ) suggest the presence of an appreciable orbital overlap and partial covalent character of the metal ligand bond. For most of the octahedral Ni(II) complexes studied in the present investigation, the ratio of first and second band is close to 1.8 which is in agreement with reported value<sup>30</sup>. All the complexes are paramagnetic. The magnetic moment value lies in the range 2.89 to 2.97 B.M. which is in expected value of octahedral Ni(II) ion.

The value of Racah parameter (B and C), crystal field splitting energy ( $D_q$ ), Slater-Condon Shortley parameters ( $F_2$  and  $F_4$ ) and neplelauxetic ratio ( $\beta$ ) for the complex calculated following the standard method<sup>31</sup> are in agreement with those of known Co(II) and Ni(II) complexes. The value is less than unity indicating partial covalency in the metal ligand bond.

The electronic spectra and magnetic moment value of Cu(II) complexes are given in Table-4. The electronic spectral of the Cu(II) complexes show one broad band in the region  $14,000\text{--}17,000\text{ cm}^{-1}$ . These complexes also possess another strong band of higher frequency region  $27,500\text{--}29,500\text{ cm}^{-1}$ . The ligand field band can be assigned to the transition  ${}^2E_g \longrightarrow {}^2T_{2g}$  in an approximately octahedral field having  $D_{4h}$  symmetry. The width and assymetry provide evidence for tetragonal distortion and John-Teller effect. The higher frequency bands arised due to charge transfer. All the complexes show magnetic moment 1.75–1.81 (BM) at room temperature.

On the basis of the foregoing observation distorted octahedral stereochemistry is suggested for Cu(II) complexes.

TABLE-4  
ELECTRONIC SPECTRAL DATA AND MAGNETIC MOMENT AT ROOM TEMP. OF  
Cu(II) COMPLEXES

S. No.	Complexes	$\mu_{\text{eff}}$ (B.M.)	Electronic spectral bands in $\text{cm}^{-1}$	Assignments
1.	$[\text{Cu}_2(\text{DCHC})_2(\text{H}_2\text{O})_4]\text{Cl}_2$	1.81	14,930 27,030	${}^2E_g \longrightarrow {}^2T_{2g}$ CT
2.	$[\text{Cu}_2(\text{DCHC})_2(\text{H}_2\text{O})_4]\text{Br}_2$	1.78	15,150	${}^2E_g \longrightarrow {}^2T_{2g}$
3.	$[\text{Cu}_2(\text{DCHC})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$	1.75	14,810 27,400	${}^2E_g \longrightarrow {}^2T_{2g}$ CT
4.	$[\text{Cu}_2(\text{DSC})_2]$	2.01	14,600 28,520	${}^2E_g \longrightarrow {}^2T_{2g}$ CT

However the cobalt(II) and nickel(II) complexes of DSC exhibit the characteristic spectra of corresponding to tetrahedral stereochemistry.

The visible spectra of  $[\text{Co}_2(\text{DSC})_2]$  suggests tetrahedral geometry for the complex. The band *ca.*  $8,200$  and  $6,600\text{ cm}^{-1}$  may be due to  ${}^4A_2(\text{F}) \longrightarrow {}^4T_1(\text{F})(\nu_1)$  and  ${}^4A_2(\text{F}) \longrightarrow {}^4T_1(\text{P})(\nu_2)$  transitions respectively. The complex possess magnetic moment of 4.04 B.M. which further confirm the tetrahedral configuration of the complex<sup>29</sup>.

The visible spectra of  $[\text{Ni}_2(\text{DSC})_2]$  show ligand field bands around *ca.* 12000,

17,000 and 25000  $\text{cm}^{-1}$  may be attributed to the transitions  ${}^3T_1(F) \rightarrow {}^3A_2(F)(v_1)$  and  ${}^3T_1(F) \rightarrow {}^3A_1(P)(v_2)$  respectively under a tetrahedral environment around Ni(II) ion. The band located at 25,000  $\text{cm}^{-1}$  may be due to charge transfer. The magnetic moment of this complex is 4.4 B.M. which is in fair arrangement with tetrahedral geometry for Ni(II) complex<sup>32</sup>.

### Thermal analysis

The thermograms of the metal complex of DCHC follow similar pattern. The  $[\text{Ni}_2(\text{DCHC})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$  starts losing water around 190°C with a weight-loss of 8.59% at 205°C corresponding to the loss of four water molecules (8.87%) in one step and supported by an endothermic peak in DTA curve. This suggests that the four water molecules are coordinated to the metal ion in a similar chemical environment<sup>33</sup>. The decomposition proceeds slowly about 265°C and the final weight loss becomes 20.16% at about 760°C which corresponds to the formation of NiO (18–78%). It is shown by a broad exothermic peak in DTA curve. The thermal behaviour corresponds to the stoichiometry suggested for the complexes. The complexes of  $\text{Co}^{2+}$ ,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$  with DCHC show the same trend.

The thermogram of the metal complexes with DSC follow similar pattern. The decomposition of these complexes starts at *ca.* 290°C and completed at 720°C. The final weight corresponds to metal oxides. This is shown by a exothermic peak between 325°C and 650°C broad in DTA curve. It may be due to decomposition of the organic ligands and subsequent slow oxidation<sup>34</sup>.

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**SANTA BARBARA, CALIFORNIA, U.S.A.**

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