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Magnetic and Spectral Studies of Co(II), Ni(II) and Cu(II) Complexes of Sulphur and Nitrogen Containing Ligand

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In present studies, 2-amino-5-methyl-1,3,4-thiadiazole was prepared and its complexes of Co(II), Ni(II) and Cu(II) are reported. These complexes were characterized by their elemental analysis, magnetic moment, infrared spectra and electronic spectra. The ligand behaves as a neutral bidentate coordinating through two nitrogen atoms. The symmetry and various crystal field parameter have also been calculated.

Key Words: Crystal field parameters, Metal(II) complexes.

INTRODUCTION

A number of complexes of various metal ions with thiazole and benzothiazole have been reported[1-4] in which ligands behave as mondentate coordinating through only nitrogen but not through sulphur. In the present work, the substituted thiadiazole ligand *i.e.*, 2-amino-5-methyl-1,3,4-thiadiazole has been chosen and with this ligand complexes of Co(II), Ni(II) and Cu(II) have been prepared and characterized.

EXPERIMENTAL

All the reagents used were of AnalR grade. The ligand was prepared by refluxing the reaction mixture containing 0.2 mol (0.07 mL) acetic acid, 0.075 mol of thiosemicarbazide (6.46 g) and 10 g of conc. sulphuric acid for 2 h with constant stirring. After refluxing, it was poured into 40 g of ice-water mixture and was neutralized with NH_4OH solution to get the desired compound which was recrystallized from boiling water.

The complexes of Co(II), Ni(II) and Cu(II) were prepared by usual method by taking the metal salts and ligands in appropriate ratio in ethanol and refluxing the content for 2 to 4 h. The resulting complexes where washed with ether and dried in air oven.

The results of elemental analysis of the ligand and its metal complexes has been given in Table-1. The infrared spectra of the complexes were taken by Perkin-Elmer diffraction gratting IR spectrophotometer in 4000-200 cm^{-1} (KBr disc).

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TABLE-1

Compound (colour)	Found (Calcd.) %						μ_{eff} (BM)
	M	C	H	N	S	Cl	
Ligand	–	31.40	4.41	36.30	27.86	–	–
(Yellowish)	–	(31.34)	(4.348)	(36.52)	(27.86)	–	
CoL_2Cl_2	16.30	20.01	2.71	23.38	17.56	19.57	4.64
(Deep blue)	(16.30)	(20.20)	(2.76)	(23.30)	(17.68)	(19.61)	
$CoL_2(NO_3)_2$	14.36	17.39	2.43	26.62	15.51	–	4.62
(Pink)	(14.24)	(14.43)	(2.42)	(27.11)	(15.49)	–	
NiL_2Cl_2	16.12	20.20	2.81	22.90	17.81	19.77	3.00
(Yellowish green)	(11.12)	(20.16)	(2.77)	(23.30)	(17.79)	(19.73)	
$NiL_2(NO_3)_2$	11.15	20.50	3.00	29.30	18.21	–	3.04
(Dark violet)	(11.12)	(20.46)	(2.84)	(29.18)	(18.19)	–	
CuL_2Cl_2	17.05	19.24	2.82	22.98	17.06	19.50	2.20
(Green)	(17.42)	(19.75)	(2.74)	(23.04)	(17.55)	(19.47)	
$CuL_2(NO_3)_2$	21.05	12.01	1.71	23.12	10.62	–	1.72
(Bluish green)	(21.02)	(11.92)	(1.65)	(23.17)	(10.59)	–	

RESULTS AND DISCUSSION

The conductivity values 14-16 om^{-1} cm^2 mol^{-1} of all the complexes were found to be too low to account for any electrolytic nature of the complexes. Co(II) complexes have magnetic moment 4.62-4.64 BM which are higher than the values due to three unpaired electrons (3.89 BM). This may be due to orbital contribution by $^4T_{1g}$ ground term in octahedral field which is triply degenerate. In the case of Ni(II) complexes, the μ_{eff} values were found to be 3.00-3.04 BM which lie within the limits specified for Ni(II) complexes in octahedral environment[5]. The value is slightly higher than the spin only value due to two unpaired electrons (2.82 BM). This is due to slight distortion from pure O_h symmetry to D_{4h} symmetry which is common in d^8 system because of Jahn Teller effect. The μ_{eff} values for Cu(II) complexes were 1.72-2.20 BM which are well within the range for octahedral Cu(II) complexes.

The infrared spectrum of the complexes in comparison with free ligand reveals the mode of coordination. The ligand absorbs at 3420 and 3287 cm^{-1} due to $\nu_{as}(NH_2)$. These bands are observed to shift towards the lower frequency in all the complexes. These bands appear at 3375-3330 and 3253-3200 cm^{-1}, respectively which shows the coordination through nitrogen of NH_2[6,7]. The possibility of resonating feature of the ligand is observed by the appearance of bands at 3080 and 2780 cm^{-1} in the spectrum of the free ligand due to ν(NH) and ν(NH + CH). These bands are also observed to be deformed and shifted significantly to lower frequency in the spectra of all the six metal complexes. These findings further support the involvement of NH_2 moiety in the complexaton without deprotonation. In finger print region of the free ligand spectrum two bands *i.e.*, at 1675 and 1632 cm^{-1} appear. The former is due to ν(NH) and the latter is due to ν(CN)[8]. The low energy band (1632 cm^{-1})

invariably moves to lower frequencies in all the complexes by 30-40 cm^{-1}. The higher frequency band either lowered or splitted up into two. These phenomenon demonstrates the coordination through both NH_2 and CN nitrogen atoms of the ligand. The coordination through azomethene nitrogen is further substaintiated by the disappearance of a band due to moiety of the ligand which absorbs at 1595 cm^{-1} in the spectrum of the ligand. The band at 685 cm^{-1} of the free ligand is assigned to C-S endocyclic. This bands moves towards higher frequency range 712-709 cm^{-1} in almost all the complexes[9,10]. It shows that the sulphur of thiadiazole ring is not participating in coordination.

The N-N band mixed with $\nu(CH_3)$ rocking and ν(C-S) contributes to the vibrations near 1070 and 817 cm^{-1}. In the spectra of the complexes of band at 1070 cm^{-1} is observed to shift towards the lower frequency by the order of 30-40 cm^{-1}. This shift signifies the involvement of only one nitrogen of N-N moiety otherwise a shift of 50 cm^{-1} or more would have occured[11].

The coordination through nitrogen is further evidenced by the appearance of the new bands in far infrared region of the spectra of the metal complexes. The new bands at 435-420 cm^{-1} may be assigned to ν(M-N). In addition to this, in chloro complexes a new band in the far infrared region at 300 cm^{-1} has been observed which is due to the ν(M-Cl). In nitrato complexes the appearance of some new bands at 1420, 1305 and 1005 cm^{-1} shows the presence of monodentate nature[12] of NO_3^-.

The electronic spectra of Co(II) complexes exhibit two bands in visible region which may be assigned as below:

$$\nu_1 = 18690\text{-}19050\ cm^{-1} \text{ due to } {}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$$

$$\nu_2 = 17860\text{-}18690\ cm^{-1} \text{ due to } {}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$$

On the basis of these two transition bands, the values of 10 Dq and B were calculated and reported. 10 Dq = 1007 cm^{-1} for chloro complexes and 10 Dq = 999 cm^{-1} for nitrato complexes. B = 721 for chloro and B = 8974 cm^{-1} for nitrato complexes. These values of the crystal field parameters well correspond to the octahedral symmetry around Co(II) with certain distortion[13,14]. The nephelauxatic effect was found to be nearly 0.80 which shows partial covalent character in the complexes.

In Ni(II) complexes, two bands have been observed in the visible region which are assigned as below:

$$\nu_1 = 15240 \text{ and } 5280\ cm^{-1} \text{ due to } {}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F) \text{ and}$$

$$\nu_2 = 25450 \text{ and } 25500\ cm^{-1} \text{ due to } {}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$$

The ν_2 = 1.66 and 1.67 which in Tanabe-Suganodiagram corresponds to Dq/B = 4.13 and 4.15. From the values of Dq/B, 10 Dq values were calcualted to be 12129 and 12160 cm^{-1} and B values were found to be 293.28 and 293 cm^{-1} for chloride and nitrate complexes, respectively. These values of crystal field parameters are in good agreement with octahedral Ni(II) complexes. The nephelauxatic effect $B = B/B_0 = 292.28/1040 = 0.28$ and $292/1040 \approx 0.28$, which suggests a goods deal of covalent character in M-L bands of these complexes of Ni(II)[15,16].

Cu(II) complexes exhibit one broad band in the visible spectrum at 15380 and 15500 cm^{-1} which may be assigned to $^2T_{2g} \leftarrow {}^2E_g$ transition. The value is quite consistent with the values obtained for distorted octahedral Cu(II) complexes[16,17].

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