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Synthesis, Spectral and Thermal Studies of Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Schiff Bases Derived from 2-Amxno-5-Aryl-1,3,4-Thiadizole

Mala Nath^a, Alok Kumar^a & Shobhna Vashistha^a ^a Chemistry Department, Roorkee University, Roorkee, -247 667, India Published online: 23 Apr 2008.

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SYNTHESIS, SPECTRAL AND THERMAL STUDIES OF Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF SCHIFF BASES DERIVED FROM 2-AMINO-5-ARYL-1,3,4-THIADIAZOLE

Mala Nath^{*}, Alok Kumar and Shobhna Vashistha

Chemistry Department, Roorkee University, Roorkee-247 667, India

ABSTRACT

Some transition metal complexes of the type $ML_2 nH_2O$ [where M = Co(II), Ni(II) and Cu(II); n = 2 and when M = Zn, n = 0; L = anion ofthe Schiff bases derived from the condensation of 2-amino-5-phenyl-1,3,4-thiadiazole with 2-hydroxy-1-naphthaldehyde (HL^{1}) or 2-hydroxyacetophenone (HL²) and derived from 2-amino-5-(2-methoxyphenyl)-1,3,4thiadiazole and 2-hydroxybenzaldehyde (HL³) or 2-hydroxyacetophenone (HL⁴)] have been synthesized and characterized by elemental analyses, molar conductance. magnetic measurements, infrared and electronic spectral studies. The analytical data show 1:2 metal to ligand stoichiometry of the complexes. Magnetic moments, along with electronic spectral data, suggest a distorted octahedral geometry for the Co, Ni and Cu complexes, whereas, a tetrahedral structure has been proposed for the Zn complexes. The presence of water molecules in the Co(II), Ni(II) and Cu(II) complexes is also indicated by the thermal studies.

INTRODUCTION

Thiadiazoles have been reported to display fungicidal properties by virtue of the -N=C-S- linkage, which is a possible toxophore in many



Fig. 1. Structure of the Schiff Bases

pesticides¹. 2,5-Disubstituted-1,3,4-thiadiazoles have been found to possess herbicidal, bacteriostatic, radioprotective and diuretic properties¹⁻³. A considerable amount of work on 1,3,4-thiadiazole has been carried out since 1960, but relatively less attention has been paid to the synthesis and structural behaviour of their Schiff bases and of their metal complexes. There are a few reports on transition metal complexes of . Schiff bases derived from 2-amino-5-aryl-1,3,4thiadiazoles⁴⁻⁷. The present communication is a part of a programme to study such complexes and deals with the synthesis and structural features of Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff bases derived from 2-amino-5-(phenyl or 2-methoxyphenyl)-1,3,4thiadiazole and different aldehydes and ketones (Fig. 1).

RESULTS AND DISCUSSION

The complexes of the general formula $ML_2 \cdot nH_2O$ (where M=Co, Ni and Cu, n=2 and when M=Zn, n=0; L=anion of the Schiff bases) were prepared by the interaction of metal acetate and Schiff base (HL) obtained by the condensation of 2-amino-5-(phenyl or 2-methoxyphenyl)-1,3,4-thiadiazole and different aldehydes or ketones according to the following equation:

Co(II), Ni(II), Cu(II), AND Zn(II) COMPLEXES

(HL = Schiff bases as indicated in Fig. 1; M = Co, Ni and Cu, n=2; M=Zn, n=0; x=2 or 4).

Schiff bases and their metal complexes are coloured and stable towards air and moisture. Schiff bases are soluble in ethanol, methanol, chloroform, benzene and acetonitrile. Their copper, cobalt, acetone. zinc complexes are sparingly soluble nickel and in acetone and chloroform but soluble in methanol and ethanol on heating. Freshly prepared samples are, however, completely soluble in dioxane and DMF. The analytical data of the Schiff bases and of their complexes are presented in Table I, which suggest that the metal to ligand ratio in all the complexes is 1:2 and the data are consistent with the assigned formulae, ML₂.nH₂O, where n = 0 for M = Zn(II) and n = 2 for M = Co(II), Ni(II) and Cu(II). Molar conductance values of the complexes (of 10⁻³ M solution) are in the range 3.60 - 15.50 ohm⁻¹ cm² mol⁻¹ (Table I) suggesting a non-electrolytic nature of the complexes. Hence, the ligands, besides being coordinated to the metal ions, also neutralise their charge.

Thermal Studies

The thermograms of the complexes show no mass loss upto $\sim 100^{\circ}$ C indicating the absence of lattice water. Sharp endothermic peaks observed in the range $162 - 240^{\circ}$ C for the complexes of Co(II), $108 - 170^{\circ}$ C for Ni(II) and $115 - 150^{\circ}$ C for Cu(II) in the DTA curves, in conjunction with the mass loss in the TG curves corresponding to two water molecules, confirm the stoichiometry ML₂.2H₂O for the Co(II), Ni(II) and Cu(II) complexes. Thereafter, the decomposition of the ligands takes place continuously upto $\sim 700^{\circ}$ C giving metal(II) oxide as residue. However, the mass loss starts at 238^o C in case of the Zn(II) complexes and continues slowly and linearly. Finally, a stable plateau

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TABLE I

Analytical Data of the Schiff Bases and their Metal Complexes

olar	cm ² mol ⁻¹	11	1	ı	, E.,	n 1 a ^{ta} r	4.51
Mc	ν ν ν	10	12.55 (12.68)	14.26 (14.23)	13.35 (13.50)	12.89 (12.91)	11.10 (111.12)
Calcd.)	H	6	3.71 (3.95)	4.15 (4.44)	4.20 (4.21)	4.35 (4.65)	3.71 (3.73)
Obsd. (U	∞ .	68.55 (68.86)	65.02 (65.06)	61.55 (61.72)	62.60 (62.75)	59,91 (60.39)
Analysis %	S	L	9.91 (9.68)	11.01 (10.86)	10.00 (10.30)	10.16 (9.85)	8.90 (8.49)
emental	M	9	1	I	t.		7.35 (7.80)
M.P. El		5	85-86	215-217	178-179	176-177	240
Colour/ Viald	(%)	4	Dull green (91)	Light yellow (57)	Yellow (56)	Yellow (64)	Dark green (46)
Formula weight(a)	weight(E)	3	331.40	295.37	311.37	325.39	755.75
Schiff base/complex		2	HL ¹ (C ₁₉ H ₁₃ N ₃ SO)	HL ² (C ₁₆ H ₁₃ N ₃ SO)	HL ³ (C ₁₆ H ₁₃ N ₃ SO ₂)	HL^4 $(C_{17}H_{15}N_3SO_2)$	Co(L ¹) ₂ , 2H ₂ O (C ₃₈ H ₂₈ N ₆ S ₂ O ₄ Co)
SI			1.	2.	. .	4.	5.

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11	3.75	6.80	10.75	12.30	14.10	15.50	8.75
10	12.50 (12.29)	11.75 (11.74)	11.00 (11.30)	11.10 (11.12)	12.10 (12.30)	11.50 (11.75)	11.35 (11.30)
6	4.03 (4.13) (3.85 (3.94) (4.35 (4.34) (3.65 (3.74) (4.03 (4.13) (3.80 (3.95) (4.25 (4.34) (
8	56.10 (56.22)	53.69 (53.71)	55.01 (54.91)	60.50 (60.41)	56.15 (56.24)	53.69 (53.73)	54.60 (54.93)
٢	9.46 (9.38)	9.04 (8.96)	8.96 (8.62)	8.90 (8.49)	9.88 (9.38)	9.13 (8.96)	9.06 (8.62)
9	8.36 (8.62)	8.33 (8.23)	8.32 (7.92)	7.42 (7.77)	8.20 (8.59)	8.42 (8.20)	8.29 (7.89)
5	248	222	198	115	108	235	229
4	Blue (49)	Blue (71)	Blue (69)	Brown (43)	Light green (55)	Light green (76)	Light green (65)
3	683.68	715.68	743.73	755.50	683.44	715.44	743.49
2	$\begin{array}{c} C_0(L^2)_{2,2}H_2O\\ (C_{32}H_{28}N_6S_2O_4C_0) \end{array}$	$C_0(L^3)_2, 2H_2O_0(C_3)_2H_{28}N_6S_2O_6C_0)$	$\begin{array}{c} Co(L^4)_{2.}2H_2O\\ (C_{34}H_{32}N_6S_2O_6C0) \end{array}$		$Ni(L^2)_2.2H_2O$ ($C_{32}H_{28}N_6S_2O_4Ni$)	Ni $(L^3)_2, 2H_2O$ ($C_{32}H_{28}N_6S_2O_6Ni$)	Ni(L ⁴) ₂ .2H ₂ O (C ₃₄ H ₃₂ N ₆ S ₂ O ₆ Ni)
1	.9	7.	×.	6	10.	11.	12.

Co(II), Ni(II), Cu(II), AND Zn(II) COMPLEXES

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(continued)

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Table. I. Continued

4.85 9.75 6.20 3.85 3.60 4.25 1 3.65 11.20 (3.71) (11.05) 12.20 (12.21) 11.50 (11.67) 11.25 (11.23) 12.00 (11.57) 12.72 (12.85) 10 4.35 (4.31) 3.12 (3.33) 4.08 (4.10) 3.85 (3.92) 3.61 (3.70) 6 60.15 (60.03) 55.75 (55.84) 53.25 (53.36) 54.71 (54.57) 58.35 (58.76) 62.70 (62.85) ∞ 10.02 (9.80) 8.90 (8.44) 9.45 (9.32) 8.75 (8.90) 9.02 (8.57) 8.96 (8.83) 7 9.75 (10.00) 8.10 (8.36) 9.23 (9.32) 8.14 (8.49) 9.00 (8.82) 8.81 (0.00) 9 Yellowish 245 brown (26) 272 160 195 225 221 Ś Green (56) White (22) Green (52) Black (54) Steel grey (60) 4 760.35 688.29 720.29 748.35 726.17 654.11 3 Cu(L¹)₂.2H₂O (C₃₈H₂₈N₆S₂O₄Cu) $Cu(L^2)_{2.2H_2O}$ $(C_{32}H_{28}N_6S_2O_4Cu)$ Cu(L³)₂.2H₂O (C₃₂H₂₈N₆S₂O₆Cu) Cu(L⁴)₂.2H₂O (C₃₄H₃₂N₆S₂O₆Cu) $Zn(L^1)_2$ ($C_{38}H_{24}N_6S_2O_2Zn$) $Zn(L^2)_2$ (C₃₂H₂₄N₆S₂O₂Zn) 3 13. 14. 15. 16. 17. 18.

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 $(X = H \text{ or } OCH_3)$

Fig. 2. Hydrogen Bonded Structure of HL

is obtained in the TG curve, corresponding to the zinc oxide. The general order of the stabilities on the basis of the DTG peak and initial decomposition temperature is : Zn > Co > Cu > Ni.

Infrared Spectra

The IR spectra of the Schiff bases exhibit a strong band at 2900 ± 25 cm⁻¹ characteristic of the intramoleculary hydrogen bonded phenolic OH vibration⁶. It is absent in the spectra of the complexes suggesting the deprotonation of the phenolic OH group on complex formation. Instead, strong and broad bands are observed in the range 3260 – 3285 cm⁻¹ indicating the presence of coordinated water molecules. A weak band at 890 ± 30 cm⁻¹ in the spectra of the complexes is perhaps due to the wagging and rocking modes of coordinated water molecules^{8,9}. The appearance of the azomethine ν (C=N) vibration in all the Schiff bases at lower frequencies (1625 ± 10 cm⁻¹), in comparison with the normal position (1675 cm⁻¹), indicates the involvement of the azomethine nitrogen atoms in hydrogen bonding (Fig. 2).

The $\nu(>C=N-N=C<)$ band of the heterocyclic ring is observed at 1575 ± 5 cm⁻¹ in the spectra of the Schiff bases⁵. The azomethine $\nu(C=N)$ vibration undergoes a shift to lower frequency (1604 ± 8 cm⁻¹) on complex formation, suggesting coordination of the azomethine nitrogen to the metal. But this vibration is overlapped with that of the $\nu(>C=N-N=C<)$ band of the heterocyclic ring and is observed as a broad band with a

shoulder in all the complexes. Other characteristic IR bands observed in the spectra of the Schiff bases at 994 \pm 8 and 760 \pm 2 cm⁻¹ have been assigned⁵ to the ν (N–N) and ν (C–S–C) modes of vibration, respectively, of the thiadiazole ring. In the spectra of all the complexes these vibrations remain almost unchanged, indicating thereby the noninvolvement of the ring nitrogen and sulphur in coordination. The IR spectra of the Schiff bases display a band at $1262 \pm 10 \text{ cm}^{-1}$, characteristic of the phenolic ν (C–O) vibration, that undergoes a shift to higher frequency in the spectra of the complexes, indicating coordination of the Schiff bases through the phenolic oxygen atom. The coordination through the oxygen and nitrogen is further supported by the occurrence of new bands in the regions 500 - 600 cm⁻¹ and 400 - 460cm⁻¹, which may be assigned^{8,10} to the ν (M–O) and the ν (M–N) vibrations, respectively, in the spectra of all complexes.

Magnetic Moments and Electronic Spectra

The magnetic moment values and the electronic spectral bands, together with the suggested assignments for the transitions in the complexes $ML_2.nH_2O$, are recorded in Table II. Comparatively higher magnetic moments than the spin-only values for the octahedral complexes are considered to be due to some orbital contributions⁴.

The magnetic moments (5.10 – 5.35 B.M.) of the cobalt(II) complexes suggest a high-spin octahedral geometry with very high orbital contributions attributable to the three-fold degeneracy of ${}^{4}T_{1g}(F)$ ground term¹¹. The observed high value of μ_{eff} of the cobalt complexes may be due to the mixing of the ground state with the excited state. The electronic spectra of the cobalt complexes show two bands at 14,800 – 14,925 and 16,340 – 17,036 cm⁻¹ which are assigned to the ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$ (ν_{2}) and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ (ν_{3}) transitions, respectively, in the octahedral environment around cobalt(II)^{8,9,12}.

The observed magnetic moments of the nickel complexes are in the range 2.53 - 2.95 B.M., close to the value required for octahedral structures with a ${}^{3}A_{2g}$ ground term¹¹. Their electronic spectra show two bands in the regions 15,500 - 17,007 and 23,981 - 26,316 cm⁻¹ assigned

to the ${}^{3}A_{2g} \longrightarrow {}^{3}T_{1g}(F)$ (ν_{2}) and ${}^{3}A_{2g} \longrightarrow {}^{3}T_{1g}(P)$ (ν_{3}) transitions, respectively¹². These bands, together with the magnetic moment values, suggest an octahedral stereochemistry for the Ni(II) complexes^{11,12}.

The magnetic moments of the Cu(II) complexes are in the range 1.93 – 1.82 B.M., indicating the presence of one unpaired electron per copper ion. Their electronic spectra show a broad envelope around 14,286 – 14,700 cm⁻¹ due to the ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition in the octahedral field. The broadening of the band may be due to the Jahn-Teller effect. The observed magnetic susceptibilities [- (3.0 to 6.0) × 10⁻⁴ cgs units] of the Zn(II) complexes indicate their diamagnetic behaviour. All the electronic spectra show a strong band in the region 230 – 260 nm (43,500 – 38,500 cm⁻¹) and a weaker band in the range 275 – 325 nm (36,400 – 30,800 cm⁻¹) which are characteristic of heterocyclic systems with extended conjugation associated with π - π^{*} transitions¹³. A band in the region 335 – 380 nm (29,900 – 26,400 cm⁻¹) may be due to the secondary band of benzene ring/intramolecular charge transfer band within the ligand moiety.

The position of ν_1 and the values of the electronic parameters such as 10 Dq and β calculated from the ν_2 and ν_3 transitions (Table II) indicate the presence of an octahedral environment around the Co(II) and Ni(II) ions, in conformity with the conclusions drawn from the magnetic moment values¹⁴. The β values for the Co(II) and Ni(II) complexes are calculated to be less than unity, indicating partial covalency in the metal-ligand bond due to the presence of appreciable orbital overlap¹⁴.

Based on the analytical results, spectral data, magnetic moments and thermal behaviour, we suggest a distorted octahedral stereochemistry for the Co(II), Ni(II) and Cu(II) complexes and tetrahedral coordination for the Zn(II) complexes (Fig. 3).

EXPERIMENTAL

Salicylaldehyde (B.D.H.), 2-hydroxyacetophenone (Merck), 2-hydroxy-1-naphthaldehyde (Fluka), thiosemicarbazide (Merck), benzaldehyde (Merck), 2-methoxybenzaldehyde (Merck), ferric chloride hexahydrate Downloaded by [Tufts University] at 10:45 17 October 2014

TABLE II

Magnetic Moments (B.M.), Electronic Transitions and Crystal Field Parameters of the Complexes

Complex	μ _{eff} (B.M.)	Electronic transitions (cm ⁻¹)	Assignments	10 Dq	B ₃₅	ß ₃₅	v2/v1	LFSC KJ/mol
1	2	3	4	5	9	7	8	6
Co(L ¹) ₂ ,2H ₂ O	5.35	$\begin{array}{c} 7067 \ (\nu_1) \\ 14925 \ (\nu_2) \\ 16807 \ (\nu_3) \end{array}$	$(\nu_1) \ {}^4 T_{1g}(F) \rightarrow {}^4 T_{2g}$	7858	702	0.72	2.11	93.88
$Co(L^2)_2, 2H_2O$	5.10	$\begin{array}{c} 6974 & (\nu_1) \\ 14925 & (\nu_2) \\ 17036 & (\nu_3) \end{array}$	$(\nu_2) \ ^4T_{1g}(F) \rightarrow {}^4A_{2g}$	7951	736	0.76	2.14	94.99
Co(L ³) ₂ , 2H ₂ O	5.20	$\begin{array}{c} 6930 (\nu_1) \\ 14800 (\nu_2) \\ 16340 (\nu_3) \end{array}$	$(\nu_3) \ ^4 T_{1g}(F) \rightarrow {}^4 T_{1g}(F)$	7870	690	0.71	2.14	94.03
Co(L ⁴) ₂ .2H ₂ O	5.15	$\begin{array}{c} 6930 (\nu_1) \\ 14805 (\nu_2) \\ 16350 (\nu_3) \end{array}$		7875	691	0.71	2.14	94.10

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-	2	3	4	5	9	2	8	6
Ni(L ¹) ₂ .2H ₂ O	2.53	$\begin{array}{c} 9354 (\nu_1) \\ 17007 (\nu_2) \\ 23981 (\nu_3) \end{array}$	$(\nu_1) \ {}^3A_{2g} \ \longrightarrow {}^3T_{2g}(F)$	9354	862	0.83	1.82	111.76
$Ni(L^2)_2.2H_2O$	2.59	$\begin{array}{c} 10662 & (\nu_1) \\ 16639 & (\nu_2) \\ 26316 & (\nu_3) \end{array}$	$(\nu_2) \ ^3\mathrm{A}_{2g} \rightarrow \ ^3\mathrm{T}_{\mathrm{lg}}(\mathrm{F})$	10662	731	0.70	1.56	127.38
Ni(L ³) ₂ .2H ₂ O	2.90	9563 (ν_1) 15500 (ν_2) 25750 (ν_3)	$(\nu_3) \ ^3A_{2g} \rightarrow {}^3T_{lg}(P)$	9563	837	0.80	1.62	114.25
Ni(L ⁴) ₂ .2H ₂ O	2.95	9847 (ν_1) 15690 (ν_2) 25350 (ν_3)		9847	767	0.74	1.59	117.65
$Cu(L^1)_2.2H_2O$	1.82	14663		ī	ı	ı	I	I
$Cu(L^2)_2.2H_2O$	1.93	14286		I	ı	I	i	I
$Cu(L^3)_2.2H_2O$	1.89	14590	$^{2}\mathrm{E_{g}}{\longrightarrow}^{2}\mathrm{T_{2g}}$	I	1	5	I	ı
$Cu(L^4)_2.2H_2O$	1.91	14700		1	ı	ı	I	ı
Zn(L ¹) ₂	Diamagnetic	ı	ł	ı	1	ı	ı	I
$Zn(L^2)_2$	Diamagnetic	1	I	1	1	1	•	

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Fig. 3. Proposed Structures of (I) $ML_2 \cdot 2H_2O$ and (II) ZnL_2 [where M = Co, Ni and Cu; NO = Coordinating sites of L].

(B.D.H.), and metal acetates (metal = Co, Ni, Cu and Zn) of Anal. R. Grade (Sarabhai M. Chemicals) were used as received. All other chemicals and solvents used were dried and purified by the standard methods, and moisture was excluded from the Other glass apparatus. physical measurements and spectral studies viz., elemental analysis, molar infrared electronic conductance. and spectra, and magnetic susceptibility measurements were carried out on the same instruments as described previously¹⁰. TG, DTG and DTA of the complexes were carried out on a Stanton-Redcroft TG 770 themobalance. Samples of ~10 mg were used for TGA and the heating rate was 5° C min⁻¹. The studies were carried out in static air at a chart speed of 20 cm hr⁻¹. Schiff bases used were synthesized by the condensation of 2-amino-5-(phenyl or 2methoxyphenyl)-1,3,4-thiadiazole with aldehyde or ketone.

Synthesis of the Schiff Bases

2-Amino-5-phenyl-1,3,4-thiadiazole 2-amino-5-(2-methoxyand phenyl)-1,3,4-thiadiazole were prepared by oxidative cyclisation of benzaldehydethiosemicarbazone 2-methoxybenzaldehydethiosemiand carbazone. respectively, using ferric chloride hexahvdrate as an oxidizing agent¹⁵. The Schiff bases were prepared by refluxing 2-amino-5-(phenyl or 2-methoxyphenyl)-1,3,4-thiadiazole (0.25 mol) and aldehyde or ketone (0.25 mol) in distilled ethanol (50.0 mL) for 2 hours.

Coloured solids were obtained on cooling after the removal of excess of solvent by distillation. They were recrystallized from the same solvent and dried under vacuum.

Synthesis of the Metal Complexes

The Schiff base (0.03 mol) in 25.0 mL of ethanol was added to a methanolic solution (20.0 mL) of metal acetate (0.015 mol) with constant stirring. The mixture was refluxed for 3 hours. Upon concentration and cooling, coloured crystals of the respective metal chelates separated out and were filtered, recrystallized from ethanol, and dried in air.

Calculations

The positions of v_1 and the values of electronic parameters of nickel and cobalt complexes were calculated using the following equations¹⁴.

For the Ni Complexes: d^8 octahedral 10 Dq = ν_1

10 Dq = $\frac{1}{34} \left[9(v_2 + v_3) \pm \left\{ 81 \left(v_2^2 + v_3^2 \right) - 178 v_2 v_3 \right\}^{1/2} \right]$ B = $(v_2 + v_3 - 3v_1)/15$

For the Co Complexes: d⁷ octahedral

10 Dq =
$$v_2 - v_1$$

10 Dq = $\frac{1}{3}(2v_2 - v_3) + 5B$
B = $\frac{1}{510} [7(v_3 - 2v_2) \pm 3\{81 v_3^2 - 16 v_2(v_2 - v_3)\}^{1/2}]$

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