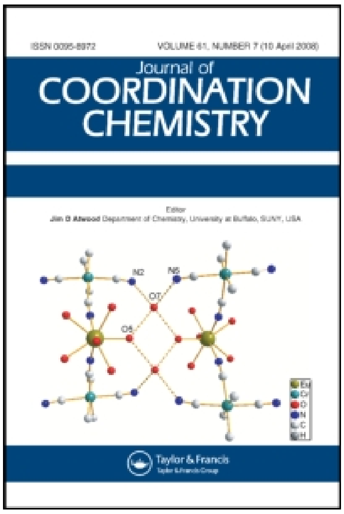

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Synthesis and spectral studies of new N_2S_2 and N_2O_2 Mannich base ligands and their metal complexes

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Synthesis and spectral studies of new N_2S_2 and N_2O_2 Mannich base ligands and their metal complexes

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New Mannich bases bis(thiosemicarbazide methyl) phosphinic acid H_3L^1 and bis(1-phenylsemicarbazide methyl) phosphinic acid H_3L^2 were synthesized from condensation of phosphinic acid and formaldehyde with thiosemicarbazide and 1-phenylsemicarbazide, respectively. Monomeric complexes of these ligands, of general formula $K_2[Cr^{III}(L^n)Cl_2]$, $K_3[Fe^{II}(L^1)Cl_2]$, $K_3[Mn^{II}(L^2)Cl_2]$, and $K[M(L^n)]$ (M = Co(II), Ni(II), Cu(II), Zn(II) or Cd(II); $n = 1, 2$) are reported. The mode of bonding and overall geometry of the complexes were determined through IR, UV-Vis, NMR, and mass spectral studies, magnetic moment measurements, elemental analysis, metal content, and conductance. These studies revealed octahedral geometries for the Cr(III), Mn(II), and Fe(II) complexes, square planar for Co(II), Ni(II), and Cu(II) complexes and tetrahedral for the Zn(II) and Cd(II) complexes. Complex formation *via* molar ratio in DMF solution has been investigated and results were consistent to those found in the solid complexes with a ratio of (M : L) as (1 : 1).

Keywords: Mannich bases; Bis(thiosemicarbazide methyl) phosphinic acid; Bis(1-phenylsemicarbazide methyl) phosphinic acid; Transition metal complexes; Structural study

1. Introduction

There has been interest in metal complexes containing N, S and/or N, O donors [1]. Thiosemicarbazide and semicarbazides have attracted special attention due to their carcinostatic properties against a spectrum of transplaced neoplasm [2] and to their activity against certain tumors [3]. Transition metal complexes of these compounds have importance due to antituberclostatic activity [4], medicinal properties [5] and use as analytical reagents in microdetermination of metal ions [6], separation of pollutants [7], and recovery of precious metals [8]. Complexes of phosphinic acid and its derivatives are also of interest due to their pharmaceutical applications and biological activity which include enzyme inhibition [9–11]. As part of our continuing efforts to

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synthesize and characterize transition metal chelates using polydentate ligands, we describe here the synthesis and spectral investigation of two Mannich bases, bis(thiosemicarbazide methyl) phosphinic acid H_3L^1 and bis(1-phenylsemicarbazide methyl) phosphinic acid H_3L^2 and some of their metal complexes. Biological activities of the prepared ligands and their metal complexes against different kinds of bacteria and fungi are currently under investigation.

2. Experimental

2.1. *Materials and methods*

All reagents were commercially available (Aldrich) and used without purification. Solvents were distilled from appropriate drying agents immediately prior to use. 1-Phenylsemicarbazide was prepared by a method published in [12].

2.2. *Physical measurements*

Elemental analyses (C, H, and N) were carried out on a Heraeus instrument (Vario EL). IR spectra were recorded as KBr or CsI discs using a Shimadzu 8300 FTIR spectrophotometer from 4000–250 cm^{-1}. Electronic spectra were measured from 200–900 nm for 10^{-3} M solutions in DMF at 25°C using a Shimadzu 160 spectrophotometer. Mass spectra obtained by positive Electron-Impact (EI) and Fast Atom Bombardment (FAB) were recorded on a VG autospec micromass spectrometer. NMR spectra (^1H, ^{13}C, COSY, ^{13}C–^1H correlated, ^{31}P NMR) were acquired in DMSO-d_6 solution using Bruker AMX400 MHz and Jeol Lambda 400 MHz spectrometers with tetramethylsilane (TMS) as an internal standard for ^1H NMR analysis and H_3PO_4 85% as an external standard for ^{31}P NMR analysis. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride was determined using potentiometer titration method on a 686-Titro processor-665 Dosimat–Metrohm Swiss. Conductivity measurements were made with DMF solutions using a Jenway 4071 digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Johnson Matthey Catalytic System Division).

3. Synthesis

3.1. *Preparation of H_3L^1*

A mixture of phosphinic acid (1.50 g, 22.73 mmol) and thiosemicarbazide (4.14 g, 45.46 mmol) in hydrochloric acid (6 N, 40 mL) was heated under reflux, then aqueous formaldehyde (37%, 1.36 g, 45.46 mmol) was added dropwise for 20 min. Heating was continued for 4 h using an oil bath at 105–110°C. The solution was concentrated under reduced pressure. After cooling to room temperature, a white solid was formed. This was dissolved in methanol (75 mL) and reprecipitated by adding 40 mL of diethyl ether. The product was filtered off and recrystalized from absolute ethanol.

Yield (4.64 g, 75%), m.p. 192–194°C. NMR data (ppm), δ_H(400 MHz, DMSO-d_6): 4.20 (4H, d, $J_{PH} = 12.1$ Hz, PCH_2), 6.20 (4H, s, $N_{(4)}$–H), 8.10 (1H, s, POH), 9.90 (4H, d, $N_{(1)}$–H, $N_{(2)}$–H); δ_C(100.63 MHz, DMSO-d_6): 48.99 (PCH_2, 2C), 181.80 (C=S, 2C); δ_P(109.3 MHz, DMSO-d_6) 17.36. The positive (EI) mass spectrum of H_3L^1 showed the parent ion peak at *m/z* 272 (100%) corresponding to (M^+) and the following fragments; 212 (32%) $(M\text{–}CSNH_2)^+$, 153 (46%) $[M\text{–}(CSNH_2)_2]^+$, 123 (13%) $[M-\{-(CSNH_2)_2+HN=NH+NH_2\}]^+$, 108 (50%) $[M-\{-(CSNH_2)_2+HN=NH+NH_2\}]^+$, 78 (25%) $[M-\{-(CSNH_2)_2+HN=NH+NH_2+CH_2NH_2\}]^+$, 64 (50%) HPO_2^+.

3.2. *Preparation of H_3L^2*

H_3L^2 was prepared in the same manner as H_3L^1, but 1-phenylsemicarbazide (6.86 g, 45.46 mmol) was used instead of thiosemicarbazide. An identical work-up procedure was employed for purification and recrystalization of the product to give H_3L^2 (6.57 g, 74%) as a yellow solid, m.p 196–198°C. NMR data (ppm), δ_H(400 MHz, DMSO-d_6): 3.20 (4H, d, $J_{PH} = 12.1$ Hz, PCH_2), 6.10 (4H, s, $N_{(4)}$–H) 6.80–7.20 (10H, m, Ar–H), 7.70 (2H, s, $N_{(2)}$–H), 7.80 (1H, s, POH); δ_C(100.63 MHz,DMSO-d_6): 48.99 (PCH_2, 2C), 149.81 ($C_{1,\ 1'}$, 2C), 120.95 ($C_{2,\ 2';\ 6,\ 6'}$, 4C), 119.01 ($C_{3,3';5,5'}$, 4C), 112.70 ($C_{4,4'}$,, 2C), 160.55 (C=O,2C). δ_P(109.3 MHz, DMSO-d_6): 20.45. The positive (EI) mass spectrum of H_3L^2 shows the parent ion peak at *m/z* 392 (100%) corresponds to (M^+) and the following fragments; 348 (35%) $(M-CONH_2)^+$, 305 (18%) $[M-(CONH_2)_2]^+$, 199 (31%) $[M-\{-(CONH_2)_2+PhN=NH\}]^+$, 108 (67%) $[M-(-CONH_2)_2+PhN=NH+C_2H_5PO_2\}]^+$, 92 (72%) $[M-\{-(CONH_2)_2+PhN=NH+C_2H_5PO_2+NH_2\}]^+$, 65 (18%) $[M-\{-(CONH_2)_2+PhN=NH+C_2H_5PO_2+NH_2+HCN\}]^+$.

3.3. *General synthesis of the complexes with H_3L^1 and H_3L^2 ligands*

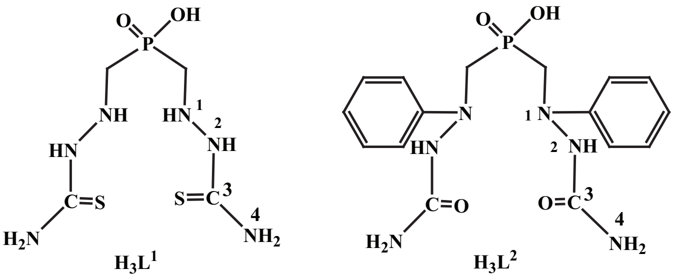
A solution of the appropriate Mannich base (1 mmol) and potassium hydroxide (3 mmol) in methanol (20 mL) was stirred for 10 min. A methanolic solution (15 mL) of the metal salt (1 mmol) (metal salts are hydrated chlorides except zinc as the anhydrous chloride) was then added dropwise. The resulting mixture was refluxed under N_2 for 2 h, resulting in the formation of a solid mass which was washed several times with hot methanol. Elemental analysis data, colors, and yields for the complexes are given in table 1.

4. Results and discussion

The Mannich bases H_3L^1 and H_3L^2 were obtained in good yields by condensation of phosphinic acid with formaldehyde (37%) and thiosemicarbazide H_3L^1 or 1-phenylsemicarbazide H_3L^2 in mole ratios of 1 : 2 : 2, respectively. The reactions were carried out in acidic medium (6N HCl) at reflux under nitrogen (scheme 1). The Mannich bases were characterized by elemental analysis (table 1), IR (table 2), UV-Vis (table 3), mass spectroscopy and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Complexes of the ligands with Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} were synthesized by

Table 1. Colors, yields, elemental analyses and molar conductance values.

			Found (Calcd) (%)					
Compound	Color	Yield (%)	M	C	H	N	Cl	Λ_M ($cm^2\Omega^{-1}mol^{-1}$)
H_3L^1	White	75	–	17.5 (17.7)	4.9 (4.8)	30.7 (30.9)		– –
$K_2[Cr(L^1)Cl_2]$	Green	63	11.8 (11.1)	10.4 (10.2)	2.3 (2.1)	17.5 (17.9)	15.9 (15.1)	148
$K_3[Fe(L^1)Cl_2]$	Brown	67	10.1 (10.9)	9.1 (9.4)	2.0 (1.9)	16.6 (16.4)	13.1 (13.8)	225
$K[Co(L^1)]$	Light red	70	16.6 (16.1)	13.3 (13.1)	2.4 (2.7)	23.0 (22.9)		110
$K[Ni(L^1)]$	Yellowish	66	16.9 (16.0)	13.3 (13.1)	2.9 (2.7)	22.7 (22.9)	–	116
$K[Cu(L^1)]$	Green	84	17.8 (17.1)	13.1 (12.9)	2.5 (2.7)	22.8 (22.6)	–	113
$K[Zn(L^1)]$	White	79	17.0 (17.5)	12.6 (12.9)	2.8 (2.7)	22.4 (22.5)	–	109
$K[Cd(L^1)]$	White	78	26.0 (26.7)	11.7 (11.4)	2.1 (2.4)	20.1 (20.0)	–	115
H_3L^2	Yellow	74	–	48.8 (49.0)	5.5 (5.4)	21.3 (21.4)	–	–
$K_2[Cr(L^2)Cl_2]$	Green	62	8.1 (8.8)	32.8 (32.5)	3.2 (3.1)	14.1 (14.2)	11.9 (12.0)	130
$K_3[Mn(L^2)Cl_2]$	Brown	73	9.0 (8.7)	30.1 (30.4)	3.0 (2.9)	13.5 (13.3)	11.9 (11.2)	210
$K[Co(L^2)]$	Red	63	11.8 (12.1)	39.7 (39.4)	3.9 (3.7)	17.1 (17.3)	–	112
$K[Ni(L^2)]$	Green	86	12.9 (12.1)	39.3 (39.5)	3.5 (3.7)	17.4 (17.3)	–	114
$K[Zn(L^2)]$	White	78	13.7 (13.3)	38.8 (38.9)	3.7 (3.6)	17.2 (17.0)	–	110
$K[Cd(L^2)]$	White	83	20.0 (20.8)	35.6 (35.5)	3.1 (3.3)	15.4 (15.5)		113



Scheme 1. General structures of Mannich bases.

heating 1 mmol of each ligand with 1 mmol of metal chloride, using methanolic potassium hydroxide as a base. Complexes of general formula $K_2[Cr^{III}(L^n)Cl_2]$, $K_3[Fe^{II}(L^1)Cl_2]$, $K_3[Mn^{II}(L^2)Cl_2]$, and $K[M(L^n)]$, (M = Co(II), Ni(II) Cu(II), Zn(II), Cd(II), or Cd(II); $n = 1, 2$) were obtained (scheme 2). The complexes are solids, stable in air and soluble in DMF and partially in DMSO (but not in other common organic solvents). The analytical data (table 1) agree well with the suggested formula. The most important infrared bands of the ligands and their complexes together with their assignments are collected in table 2.

Table 2. IR frequencies (cm^{-1}) of the compounds.

Compound	ν(C=C) Aromatic	ν_{as}(N–H), ν_s(N–H)	ν(P–C)	ν(M–N)	ν(M–O)	ν(M–S)
H_3L^1	–	3540, 3450	1420	–	–	–
$K_2[Cr(L^1)Cl_2]$	–	3510, 3382	1332	437	–	385
$K_3[Fe(L^1)Cl_2]$	–	3410, 3300	1337	459	–	376
$K[Co(L^1)]$	–	3515, 3382	1332	437	–	385
$K[Ni(L^1)]$	–	3400, 3244	1390	441	–	366
$K[Cu(L^1)]$	–	3400, 3290	1390	480	–	392
$K[Zn(L^1)]$	–	3400, 3300	1353	495	–	354
$K[Cd(L^1)]$	–	3400, 3290	1380	480	–	392
H_3L^2	1600, 1550	3325, 3275	1440	–	–	–
$K_2[Cr(L^2)Cl_2]$	1600, 1575	3450, 3398	1434	400	511	–
$K_3[Mn(L^2)Cl_2]$	1600, 1560	3500, 3350	1434	402	511	–
$K[Co(L^2)]$	1595, 1550	3400, 3244	1390	416	516	–
$K[Ni(L^2)]$	1595, 1550	3410, 3252	1390	443	518	–
$K[Zn(L^2)]$	1595, 1552	3420, 3251	1390	443	518	–
$K[Cd(L^2)]$	1595, 1550	3410, 3244	1390	414	516	–

ν(P–OH) $H_3L^1 = 2670$, $H_3L^2 = 2690$; ν(M–Cl) $K_2[Cr(L^1)Cl_2] = 281$, $K_3[Fe(L^1)Cl_2] = 285$, $K_2[Cr(L^2)Cl_2] = 287$, $K_3[Mn(L^2)Cl_2] = 285\,cm^{-1}$.

4.1. *NMR and IR spectra*

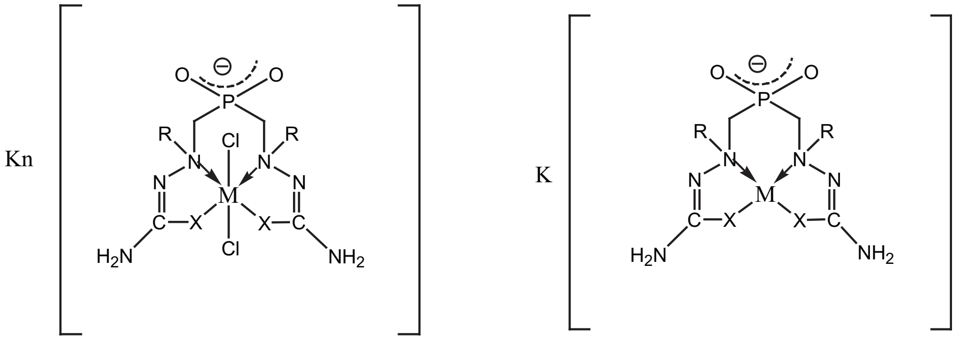
The structural information of the ligands can be deduced from NMR spectra. The ^1H, ^{13}C, and ^{31}P NMR spectra of the ligands displayed signals corresponding to the various proton, carbon, and phosphorus nuclei (section 3). The ^1H NMR spectrum of the complex $K[Ni^{II}(L^1)]$ in DMSO-d_6 showed the absence of the signal due to $N_{(2)}{-}H$ which was observed in the spectrum of H_3L^1 at 9.90 ppm suggesting deprotonation of $N_{(2)}{-}H$ upon coordination. The spectrum showed other peaks which are shifted slightly downfield and observed at 4.31 (4H, d, $J_{PH} = 11.9$ Hz, PCH_2), 6.27 (4H, s, $N_{(4)}{-}H$), and 8.47 (2H, s, $N_{(1)}{-}H$) ppm. The NMR spectrum confirms the diamagnetism of the nickel complex. IR spectra of the free Mannich bases show characteristic bands due to the ν(C=O), ν(C=S), ν(C=C), ν(P–OH), and ν(N–H) functional groups. The distinct frequency around 1420–1440 cm^{-1} assigned for ν(P–C) confirms formation of the Mannich base [13–15]. In the spectra of H_3L^1 complexes, coordination *via* thiolate sulfur is indicated by the absence of ν(C=S) (observed at 1300 cm^{-1} in free ligand) with appearance of new bands around 1658–1610 and 680–617 cm^{-1} attributed to the ν(C=N) and ν(C–S), respectively [16, 17]. The spectra of the complexes also exhibited bands around 495–437 and 385–354 cm^{-1} which could be assigned to ν(M–N) and ν(M–S), respectively. Additional bands around 285–281 cm^{-1} in $K_2[Cr^{III}(L^1)Cl_2]$ and $K_3[Fe^{II}(L^1)Cl_2]$ are assigned to ν(M–Cl) vibrations [18, 19]. The IR spectra of the complexes of H_3L^2 did not exhibit ν(C=O) which was observed in the spectrum of the free Mannich base at 1680 cm^{-1}. This is consistent with enolisation of the (C=O) group followed by deprotonation and complexation to the metal. Two bands were observed around 1149–1118 and 1658–1652 cm^{-1}, attributed to ν(C–O) and ν(C=N), respectively [20, 21]. At lower frequency the complexes exhibited bands around 518–511, 443–400, and 287–285 cm^{-1} assigned to ν(M–O), ν(M–N), and ν(M–Cl), respectively [20]. Due to the larger dipole moment change for M–O compared to M–N, the ν(M–O) usually appears at higher frequency than the ν(M–N) band [17, 22].

Table 3. Magnetic moment and UV-Vis spectral data in DMF.

Compound	μ_{eff} (BM)	Band position, (λ, nm)	Extinction coefficient $\varepsilon_{\max}$ (dm^3 mol^{-1}cm^{-1})	Assignments
$K_2[Cr(L^1)Cl_2]$	3.84	313	1100	$\pi \rightarrow \pi^*$
		370	600	CT
		303	–	$^4A_2g^{(F)} \rightarrow {}^4T_1g^{(P)}$ (υ_3) (Calcd)
		450	220	$^4A_2g^{(F)} \rightarrow {}^4T_1g^{(F)}$ (υ_2)
		630	170	$^4A_2g^{(F)} \rightarrow {}^4T_2g^{(F)}$ (υ_1) ($10D_q$)
$K_3[Fe(L^1)Cl_2]$	5.10	317	900	$\pi \rightarrow \pi^*$
		370	470	CT
		540	180	$T_2g \rightarrow A_1g$
		665	180	$^5T_2g \rightarrow {}^5Eg$
$K[Co(L^1)]$	1.80	315	1700	$\pi \rightarrow \pi^*$
		375	900	CT
		510	300	$^2Eg^{(G)} \rightarrow {}^2T_2g, {}^2T_2g^{(G)}$
		660	250	$^2Eg^{(G)} \rightarrow {}^4T_1g^{(F)}$
$K[Ni(L^1)]$	Diamagnetic	312	1600	$\pi \rightarrow \pi^*$
		380	1200	CT
		550	200	$^1A_1g \rightarrow {}^1B_1g$
$K[Cu(L^1)]$	1.87	317	1700	$\pi \rightarrow \pi^*$
		369	750	CT
		530	250	$^2B_1g \rightarrow {}^2Eg$
		640	200	$^2B_1g \rightarrow {}^2B_2g$
		810	250	$^2B_1g \rightarrow {}^2A_2g$
$K[Zn(L^1)]$	Diamagnetic	314	1000	$\pi \rightarrow \pi^*$
		380	220	CT
$K[Cd(L^1)]$	Diamagnetic	320	1450	$\pi \rightarrow \pi^*$
		400	250	CT
$K_2[Cr(L^2)Cl_2]$	3.85	302	780	$\pi \rightarrow \pi^*$
		350	410	CT
		318	–	$^4A_2g^{(F)} \rightarrow {}^4T_1g^{(P)}$ (υ_3) (Calcd.)
		500	200	$^4A_2g \rightarrow {}^4T_1g^{(F)}$ (υ_2)
		685	180	$^4A_2g \rightarrow {}^4T_2g^{(F)}$ (υ_1) ($10D_q$)
$K_3[Mn(L^2)Cl_2]$	5.39	304	350	$\pi \rightarrow \pi^*$
		340	180	CT
		455	80	$^6A_1g \rightarrow {}^4T_2g^{(G)}$
		660	60	$^6A_1g \rightarrow {}^4T_1g^{(G)}$
$K[Co(L^2)]$	1.81	302	1300	$\pi \rightarrow \pi^*$
		430	180	$^2Eg \rightarrow {}^2T_1g, {}^2T_2g$
		555	150	$^2Eg \rightarrow {}^4T_1g^{(F)}$
$K[Ni(L^2)]$	Diamagnetic	293	910	$\pi \rightarrow \pi^*$
		435	170	CT
		550	160	$^1A_1g \rightarrow {}^1A_2g$
$K[Zn(L^2)]$	Diamagnetic	305	340	$\pi \rightarrow \pi^*$
		400	50	CT
$K[Cd(L^2)]$	Diamagnetic	315	2050	$\pi \rightarrow \pi^*$
		360	800	CT

4.2. *Mass spectra*

The mass spectra were also consistent with the proposed structural formula (see section 3). The positive ion FAB mass spectrum for $K[Co^{II}(L^1)]$ showed several peaks corresponding to successive fragmentation of the molecule. The first high intensity peak observed at *m*/*z* 367 represents the molecular ion peak of the complex. Two distinct peaks were observed in the mass spectrum at *m*/*z* 137 and 59 and can be assigned to the



***n* = 2 when M = Cr(III)**
***n* = 3 when M = Mn(II), Fe(II)**

M = Co(II),Ni(II),Cu(II),
Zn(II), Cd(II)

X = S, R = H, H_3L^1
X = O, R = Ph, H_3L^2

Scheme 2. Proposed structures of metal complexes.

($CoNS_2$) fragment and the final metal residue (Co). These results are similar to analogous complexes reported earlier [23].

4.3. *Electronic spectra, magnetic moments, and conductivity measurements*

The electronic spectra of H_3L^1 complexes exhibited various extents of bathochromic shift of the bands related to the intraligand $\pi \rightarrow \pi^*$ transition (table 3). Bands related to the (CT) transition were observed as shoulders on the ligand band in the spectra of the Cr(III), Co(II), Ni(II), and Cu(II) complexes (table 3). The electronic spectrum of the Cr(III) complex displayed three additional bands, which could be attributed to the spin allowed d–d transitions [24–26]. These data together with the magnetic moment indicate an octahedral geometry around Cr(III) [27]. The band $^4A_2g^{(F)} \rightarrow {}^4T_1g^{(P)}$ (ν_3) transition may be at higher frequency and hidden by the CT or ligand band [24]. The Fe(II) complex showed the $\pi \rightarrow \pi^*$ transition plus two additional bands which could be attributed to spin allowed transitions in octahedral geometry [24–26]. The magnetic moment of this complex is typical for a high spin octahedral structure. The low magnetic moment values of the light red Co(II) complex and the green Cu(II) complex, as well as the other analytical data, are in agreement with square planar structures [24–26, 28–30]. The two complexes gave a dark brown color in DMF solutions, indicating further coordination to solvent molecules. Thus, the spectrum of the Co(II) complex in DMF exhibited two low intensity bands which are characteristic of low spin octahedral Co(II) complexes [24–26]. The spectrum of the Cu(II) complex in DMF displayed bands characteristic of distorted octahedral Cu(II) complexes. The Ni(II) complex is diamagnetic suggesting square planar geometry. The electronic spectrum of this complex was consistent with this assignment.

The spectra of the Zn(II) and Cd(II) complexes exhibited bands assigned to ligand $\pi \rightarrow \pi^*$ and M → L charge transfer [24]. Both complexes are diamagnetic as expected and normally prefer tetrahedral coordination. The molar conductivity values of the Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes were in the range 116–109 $cm^2\ \Omega^{-1}\ mol^{-1}$ indicating 1 : 1 electrolytes, while those of the Cr(III) and Fe(II) complexes were consistent with 2 : 1 and 3 : 1 electrolytes, respectively (table 1) [31]. The electronic spectra of the Cr(III) and Co(II) complexes of H_3L^2 showed no change in the position of the $\pi \rightarrow \pi^*$ ligand band, while those of the Mn(II), Zn(II), and Cd(II) complexes showed bathochromic shifts and the spectrum of Ni(II) showed hypsochromic shift (table 3). The spectra of the Cr(III) and Ni(II) complexes of H_3L^2 showed similar behavior to those of H_3L^1, suggesting octahedral geometries for Cr(III) and square planar geometry for Ni(II). The spectrum of Mn(II) complex showed three additional bands attributed to the (CT) and spin forbidden transitions in an octahedral geometry [24–26]. The red Co(II) complex gave dark brown solution in DMF indicating further coordination of Co(II) to solvent. This behavior, in addition to the value of μ_{eff} (table 3) and other analytical data, confirm square planer geometry around Co(II) [24–26, 28–30]. The spectrum of Co(II) complex in DMF showed two absorption bands in the visible region assigned to transitions of low spin octahedral Co(II) complexes [25, 26]. The molar conductivities indicate that the Cr(III) is a 2 : 1 electrolyte, while the Mn(II) complex is 3 : 1 and the rest are 1 : 1 electrolytes (table 1) [31].

4.4. *Molar ratio*

Complex formation by molar ratio of ligand to metal ion was also studied in DMF. A series of solutions containing constant concentration of metal ion (1×10^{-3} M) was treated with the same volumes of various concentrations of ligands in presence of potassium hydroxide and heated at 100°C. The results of L : M titrations were obtained by plotting absorbance of solution mixtures at $\lambda_{\max}$ of the complexes against [L]/[M] which showed a 1 : 1 M : L ratio for all the complexes, as observed for the solid state.

5. Conclusion

In this article we have explored the synthesis and coordination chemistry of some monomeric complexes obtained from the reaction of the tetradentate Mannich-base ligands H_3L^1 and H_3L^2 with metal ions. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. Complex formation study *via* molar ratio has been investigated and results were consistent to those found in the solid complexes with a ratio of M : L as 1 : 1.

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