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Metal complexes of a new class of polydentate Mannich bases: Synthesis and spectroscopic characterisation

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ABSTRACT

A new class of polydentate Mannich bases featuring an N_2S_2 donor system, bis((2-mercapto-*N*-pheny-lacetamido)methyl)phosphinic acid H_3L^1 and bis((2-mercapto-*N*-propylacetamido)methyl)phosphinic acid H_3L^2 , has been synthesised from condensation of phosphinic acid and paraformaldehyde with 2-mercaptophenylacetamide W1 and 2-mercaptopropylacetamide W2, respectively. Monomeric complexes of these ligands, of general formula $K_2[Cr^{III}(L^n)Cl_2]$, $K_3[M'^{II}(L^n)Cl_2]$ and $K[M(L^n)]$ (M' = Mn(II) or Fe(II); M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) or Hg(II); n = 1, 2) are reported. The structures of new ligands, 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 Ni(II) and Cu(II) complexes and tetrahedral for the Co(II), Zn(II), Cd(II) and Hg(II) complexes. Complex formation studies *via* molar ratio in DMF solution were consistent to those found in the solid complexes with a ratio of (M:L) as (1:1).

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1. Introduction

The design and study of complexes with N₂S₂ ligands is an interesting area of research for both inorganic and bioinorganic chemists [1,2]. Compounds bearing N and S donors have been extensively investigated with regard to their numerous applications in different fields including organic synthesis [3]. The soft-hard nature of ligands with N and S donor atoms facilitate the coordination of these ligands with a wide range of metal ions which have a potential applications in biomedical [4-6], biomimetic [7] and catalytic system [8,9]. One significant application of complexes with N₂S₂ ligands is their use in the medical fields for therapeutic and diagnostic purposes [10]. These include the complexation of N₂S₂ system with a range of soft metals such as ⁶⁴Cu, and ^{99m}Tc in diagnostic imaging and ^{186/188}Re in targeted radiotherapy [11,12]. In addition, aliphatic N₂S₂ chelates of hard metals such as ^{67/68}Ga and ¹¹¹In radionuclides are widely used in diagnostic imaging [13]. Furthermore, N₂S₂ ligands played a vital role in the development of metal-sulfur complexes with characteristic redox properties. These involve the design and synthesis of polydentate ligands with sulfur and nitrogen cores to achieve a metal environment in simple complexes directly analogous to the biological

* Corresponding author. *E-mail address:* mohamadaljeboori@yahoo.com (M.J. Al-Jeboori). system [14-16]. There has been great interest in designing complexes with N₂S₂ system that may serve as become functional models (biomimetics) of the active sites of the metalloenzymes. These covered the preparation of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with N₂S₂ donor ligands. The choice of these metals was governed by their relevance in the active sites of various oxygenases and peroxidises and their ability to react with CO₂, CO, NO or CH₃ moieties [7,17,18]. Compounds of phosphinic acid and its derivatives are also of interest due to their pharmaceutical applications and biological activity which include enzyme inhibition [19–21]. Recently, we have investigated the preparation of the potentially tetradentate Mannich base ligands system and their metal complexes [22,23]. These ligands system based on the use of semi- and thiosemicarbazide derevatives to prepare the Mannich ligands, Scheme 1. As part of our continuing efforts to synthesis and characterise transition metal chelates using polydentate ligands, we were interested to see if amide derivatives could be used to obtain new type of Mannich bases could form metal complexes with the ligands coordinated in the required fashion. The ligands have been specifically designed in which a tetradentate chelate N₂S₂ system could be used to bind metal ion upon complex formation. We describe here the synthesis and spectral investigation of two Mannich bases, bis((2-mercapto-N-phenylacetamido)methyl)phosphinic acid H₃L¹ and bis((2-mercapto-N-propylacetamido)methyl)phosphinic acid H_3L^2 (see Scheme 2) and some of their metal complexes.



Note



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$$H_{3}L^{4} = X = O, R = phenyl, R'= H$$

Scheme 1. Chemical structure of Mannich bases derived from semi- and thiosemicarbazide compounds.

2. Experimental

2.1. Materials

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

2.2. Physical measurements

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). 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-665Dosimat-Metrohm Swiss). Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. IR spectra were recorded as KBr or CsI discs using a Shimadzu 8300 FTIR spectrophotometer in the range (4000–250) cm⁻¹. Electronic spectra were measured in the region (200–900) nm using 10^{-3} M solutions in DMF at 25 °C using a Shimadzu 160 spectrophotometer. Mass spectra were obtained by positive Electron-Impact (EI) and Fast Atom Bombardment (FAB) was recorded on a VG autospec micromass spectrometer. NMR spectra (¹H, ¹³C, COSY, ¹³C–¹H correlated, ³¹P NMR) were acquired in

DMSO- d_6 solution using Brucker AMX 400 MHz and Jeol Lambda 400 MHz spectrometers with tetramethylsilane (TMS) as an internal standard for ¹H NMR analysis and H₃PO₄ 85% as an external standard for ³¹P{¹H} NMR analysis. 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 (Jonson Mattey Catalytic System Division).

3. Synthesis

3.1. Preparation of 2-mercaptophenylacetamide W1

A 100 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 2-mercaptoacetic acid (0.38 mL, 5.5 mmol). The content of the flask was cooled to about $(-5 \circ C)$ in an ice-bath. Aniline (0.5 mL, 5.5 mmol) was added dropwise, while stirring over a period of 30 min, and a white viscous liquid was formed. Un-reacted starting materials and water were removed under vacuum, and then the oil product was stored at 4 °C for 2 weeks to give a white solid. Yield: (0.63 g, 80%), mp 93–94 °C. IR data (cm⁻¹), 3315, 3283 v(N–H), 2583 v(S–H), 1659, 1620 v(C=O), 1611 δ(N-H), 1601, 1540 v(C=C), 1203 v(C-N), 1025 v(C-S). NMR data (ppm), $\delta_{\rm H}$ (400 MHz, DMSO-d₆) showed trans: cis-phenylacetamide isomers in the ratio ca. 90:10; trans isomer 90%; trans isomer; 3.4 (1H, t, J_{HH} 7.4 Hz, S-H); 3.8 (2H, d, J_{HH} 7.6 Hz, C₁-H); 7.1 (1H, dd J_{HH} 7.6 Hz, C₆-H), 7.3 (2H, d, J_{HH} 8.5 Hz, C_{5.7}-H), 7.7 (2H, d, J_{HH} 8.5 Hz, C_{4.8}-H), 10.83(1H, s, N-H); cis isomer 10%; 3.1 (1H, S-H); 3.2 (2H, C₁-H); 6.5 (Ar-H), 6.6 (Ar-H), 6.9 (Ar-H); δ_C (100.63 MHz, DMSO-d₆): 28.3 (C₁), 119.6 (C_{4.8}), 123.6 (C₆), 129.0 (C_{5.7}), 138.4 (C₃), 148.4 (C₂, C=O; cis isomer), 166.7 (C₂, C=O; trans isomer). The positive (EI) mass spectrum of W1 showed the parent ion peak at m/z 167.15 (42.30%) corresponding to (M)⁺ and the following fragments; 139.4 (22%) $[M-(C=0)]^+$, 91.4 (100%) $[M-\{(C=0)+HNCH_2SH)\}]^+$.

3.2. Preparation of 2-mercaptopropylacetamide W2

The method used to prepare 2-mercaptopropylacetamide was similar to that used for 2-mercaptophenylacetamide but propylamine (0.5 mL, 8.4 mmol) was used in place of aniline. The quantities of other reagents used were adjusted accordingly. An identical work-up procedure was employed to give (0.61 g, 84%) of the title compound as yellow oil. IR data (cm⁻¹), 3384(b) v(N–H), 2557 v(S–H), 1640, 1602 v(C=O), 1589 δ (N–H), 1201 v(C–N), 1049 v(C–S). NMR data (ppm), $\delta_{\rm H}$ (400 MHz, DMSO-d₆) showed



Scheme 2. Synthesis route of ligands.

trans:cis-acetamide isomers in the ratio 87:13; *trans* isomer 87%; 0.9 (3H, t, J_{HH} 7.6, C_5-H); 1.6 (2H, m, C_4-H); 2.7 (2H, dd, J_{HH} 7.6 Hz, C_3-H); 3.0 (1H, t, J_{HH} 7.4 Hz, S-H); 3.5 (2H, t, J_{HH} 7.6 Hz, C_1-H); 8.3 (1H, s, N-H); *cis* isomer 13%; 0.8 (C_5-H); 1.6 (C_4-H); 3.0 (C_3-H); 3.4 (d, C_1-H); 4.7 (N-H); δ_C (100.63 MHz, DMSO-d₆): *trans* isomer 87%; 11.5 (C_5), 21.1 (C_4), 40.2 (C_3), 43.7 (C_1), 172.2 (C=O, C_2); *cis* isomer 13%; 11.9 (C_5), 22.8 (C_4), 41.0 (C_3), 43.9 (C_1), 168.5 (C=O, C_2). The positive (EI) mass spectrum of W2 showed the parent ion peak at m/z 133.16 (14.70%) corresponding to (M)⁺ and the following fragments; 100.75 (6.3%) (M-SH)⁺, 85.5 (100%) [M-(SH+CH₃)]⁺, 38.4 (61.76%) [M-(SH+CH₃+CH₅NO)]⁺.

3.3. Preparation of H_3L^1

A mixture of phosphinic acid (0.52 g, 8.00 mmol) and 2-mercaptophenylacetamide (3.5 g, 16 mmol) in (1 mL HCl 37%, 40 mL EtOH) was heated under reflux, then paraformaldehyde (0.5 g. 16 mmol) was added dropwise over 20 min. The reaction was allowed to reflux for 3-4 h. The solution was concentrated under reduced pressure and a white solid was formed. This was recrystallised from methanol/diethylether, and the white solid formed was collected and dried under vacuum. Yield (5.3 g, 63%), mp 188–189 °C. NMR data (ppm), $\delta_{\rm H}$ (400 MHz, DMSO-d₆): 2.5 (2H, m, S-H), 3.3 (4H, d, J_{PH} 18.4 Hz, PCH₂), 4.1 (4H, C_{1.1'}-H), 6.7 (2H, m, C_{6.6'}-H), 7.0 (4H, m, C_{5.5':7.7'}-H), 7.2 (4H, m, C_{4.4':8.8'}-H), 10.30 (1H, s, POH); δ_C (100.63 MHz, DMSO-d₆): 32.2 (C₁), 54.8 (d, J_{PH} 40 Hz, PCH₂), 113.4 (C_{4,4';8,8'}), 128.9 (C_{5,5';7,7'}), 133.4 (C_{6,6'}), 145 (C_{3,3'}), 170.0 (C=0, 2C); δ_P (109.3 MHz, DMSO-d₆): 26.5. The positive (EI) mass spectrum of H₃L¹ showed the parent ion peak at m/z 424.02 (20.68%) corresponding to (M)⁺ and the following fragments: 396 (48.37%) (M-CH₂CH₂)⁺, 340 (36%) [M-{(CH₂CH₂)+ $(O=CCH_2CH_2)]^+$, 250 (80%) $[M-{(CH_2CH_2)+(O=CCH_2CH_2)+}$ (NPh)]⁺, 221.9 (100%) [M-{(CH₂CH₂)+(O=CCH₂CH₂)+(NPh)+ (C=O)}]⁺, 158 (22%) [M-{(CH₂CH₂)+(O=CCH₂CH₂)+(NPh)+(C=O)+ $(HOP=O)\}]^+$.

3.4. Preparation of H_3L^2

 H_3L^2 was prepared in the same manner as H_3L^1 , but 2-mercaptopropylacetamide (3.0 g, 22.0 mmol) was used instead of 2-mercaptophenylacetamid. The quantities of other reagents used were adjusted accordingly. An identical work-up procedure was employed for purification and recrystallisation of the product to give (5.8 g, 73%) of H_3L^2 as a pale yellow solid, mp 156–158 °C. NMR data (ppm), $\delta_{\rm H}$ (400 MHz, DMSO-d₆): 1.1 (6H, t, C_{5, 5'}-H), 1.5 (4H, m, C_{4, 4'}-H), 2.6 (2H, t, J_{HH} 8.1 Hz, S-H), 3.3 (4H, m, C₃, _{3'}-H), 3.5 (4H, d, J_{PH} 20.1 Hz, PCH₂), 4.4 (4H, d, C_{1, 1'}-H), 7.5 (1H, s, POH); δ_C (100.63 MHz, DMSO-d₆): 11.0 (C_{5,5'}), 20.1 (C_{4,4'}), 31.3 $(C_{1,1'})$, 49.8 (d, J_{PC} 38.3 Hz, $C_{2,2'}$), 49.8 $(C_{3,3'})$, 169.8 (C=0, 2C); δ_P (109.3 MHz, DMSO-d₆): 0.52. The positive (EI) mass spectrum of H_3L^2 shows the parent ion peak at m/z 356.41 (13.43%) corresponds to $(M)^+$ and the following fragments: 302.5 (13%) (M-NCHCO)⁺, 301.5 (33%) [M-(NCHCO+CH₂)]⁺, 287.3 (19%) [M-{(NCHCO+CH₂)+(OPOH)}]⁺, 221 (10%) [M-{(NCHCO+CH₂)+ (OPOH)+(HSCH₂CO)}]⁺, 159 (16%) [M-{(NCHCO+CH₂)+(OPOH)+ $(HSCH_2CO)+(CH_3CH_2SH)\}]^+$, 128.2 (100%) $[M-{(NCHCO+CH_2)}]^+$ $+(OPOH)+(HSCH_2CO)+(CH_3CH_2SH)+(CH_3OH)]^+$.

3.5. 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 (3.3 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 N₂ for 2 h, resulting in the formation of a solid mass which was washed several times with hot methanol. Elemental analysis data, colours, and yields for the complexes are given in (Table 1).

NMR data (ppm): K[Zn(L¹)]; the ¹H and ³¹P{¹H} NMR spectra of the complex; $\delta_{\rm H}$ (400 MHz, DMSO-d₆): 7.6–7.3 (4H, d, 12 Hz, C_{4.4';8.8'}–*H*); 7.2–6.9 (4H, dd, 12 Hz, C_{5.5';7.7'}–*H*), 7.6 (2H, t, C_{6.6'}–*H*); 3.6 (4H, d, *J*_{PH} 22.4 Hz, PCH₂); 3.4 (4H, s, C_{1, 1'}–*H*); $\delta_{\rm P}$ (109.3 MHz, DMSO-d₆): 51.

K[Zn(L²)]; the ¹H and ³¹P{¹H} NMR spectra of the complex; $\delta_{\rm H}$ (400 MHz, DMSO-d₆): 3.5 (4H, d, $J_{\rm PH}$ 24.4 Hz, PCH₂); 3.1 (4H, s, C_{1, 1}'-H); 1.5 (4H, m, C_{3, 3}'-H); 1.2 (4H, m, C_{4, 4}'-H); 0.8 (6H, m, C_{5, 5}'-H); $\delta_{\rm P}$ (109.3 MHz, DMSO-d₆): 25.

4. Results and discussion

The compounds, 2-mercaptophenylacetamide W1 and 2-mercaptopropylacetamide W2 were obtained in high yield from the reaction of 2-mercaptoacetic acid with aniline and N-propylamine, respectively. The compounds were characterised by elemental analysis, IR, ¹H, ¹³C NMR and mass spectra. IR and NMR spectral data revealed the exists of two isomers (the cis form I and the trans form II) in the solid state and in solutions (Scheme 3). The Mannich bis((2-mercapto-*N*-phenylacetamido)methyl)phosphinic bases. acid H_3L^1 and bis((2-mercapto-N-propylacetamido)methyl)phosphinic acid H₃L² were obtained in good yields from condensation of phosphinic acid and paraformaldehyde with 2-mercaptophenylacetamide and 2-mercaptopropylacetamide, respectively (Scheme 2). Monomeric complexes of the two ligands with Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} Cd^{II} and Hg^{II} were synthesised by heating 1 mmole of each ligand with 1 mmole of metal chloride, using methanolic potassium hydroxide as a base. No reaction occurred with the ligands in the absence of a base and only an intractable mixture was recovered by using 2 equivalents of base (potassium hydroxide). The choice of base was also important, and no pure complexes could be isolated using sodium acetate- or triethylamine-methanol mixture. Complexes of general formulae $K_2[Cr^{III}(L^n)Cl_2], K_3[M'^{II}(L^n)Cl_2]$ and $K[M(L^n)]$ (M' = Mn(II) or Fe(II); M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) or Hg(II); n = 1, 2) were obtained (Scheme 4). The complexes are solids, stable in air and soluble in DMF and DMSO (but not other common organic solvents). The analytical data (Table 1) agree well with the suggested formulae. The molar conductivities indicate that the Cr(III) complexes are a 2:1 electrolyte, while the Mn(II) and Fe(II) complexes are 3:1 electrolytes and the rest are 1:1 electrolytes (Table 1) [24].

4.1. IR spectra

The IR spectra of the W1 and W2 show characteristic bands due to the v(N–H), v(S–H), δ (N–H), v(C=O), and v(C–N) functional groups. The IR spectra show bands originating from the amide groups were split. The amide stretching band v(C=0) for W1 and W2 appear as a doublet of almost equally intense bands at 1659, 1620 and 1640, 1602 cm^{-1} , respectively. This may be due to the fact that the vibration mode is strongly affected by the presence of intermolecular hydrogen bonds (Scheme 5), the bands at 1659 and 1640 cm⁻¹ was assigned to relatively free carbonyl groups and the peaks at 1620 and 1602 cm⁻¹ to the hydrogen bonded ones [25], and/or resulted from the exists of two isomers in the solid state; the cis form I and the trans form II, (Scheme 3). The IR spectra of the free Mannich bases show characteristic bands at 2440, 1645–1660 and 1029–1035 cm⁻¹ due to the v(P–OH), v(C=O) and v(C-S) functional groups, respectively. The distinct frequency at ca. 1410 cm⁻¹ assigned for v(P-C) band confirms formation of the Mannich bases [26-28]. While the frequency around 2545–2619 cm⁻¹ assigned for v(S-H) band confirms presence of

Table 1

Colours, yields, elemental analyses, and molar conductance values.

Compound	Colour	Yield (%, g)	mp (°C)	Found (Calcd.) (%)			$\Lambda_{\rm M}~({ m cm}^2~\Omega^{-1}~{ m mol}^{-1})$		
				М	С	Н	Ν	Cl	
WI	Pale yellow	80, 0.63	93-94	-	57.3	5.1	8.1		-
					(57.5)	(5.3)	(8.4)	-	
H_3L^1	White	63, 5.3	163-165	-	51.2	4.7	6.5	-	-
- W. 1					(50.9)	(4.9)	(6.6)		
$K_2[Cr^m(L^1)Cl_2]$	Blue	68, 0.41	273-275*	8.1	35.1	2.7	4.6	11.1	155.4
	P		044 045	(8.3)	(34.7)	(2.9)	(4.5)	(11.4)	227.0
$K_3[Mn''(L')Cl_2]$	Brown	77.3, 0.5	311-31/*	8.5	31.9	2.8	4.1	11.1	237.9
	Deals and		255 250*	(8.3)	(32.5)	(2.7)	(4.2)	(10.7)	221.1
$K_3[Fe-(L+)Cl2]$	Dark red	76.5, 0.5	255-258	8.2	32.7	3.1	4.3	10.5	221.1
K[Coll(I ¹)]	Pad brown	70404	244 246	(0.4)	(52.4)	(2.7)	(4.2)	(10.0)	105
	Red-DIOWII	79.4, 0.4	244-240	(11.2)	(41.6)	5.I (2.4)	5.0 (5.4)	-	105
$K[N;II(1^{1})]$	Creen	597031	266_260*	(11.5)	(41.0)	(3.4)	(3.4)		107.2
	Gitti	55.7, 0.51	200-205	(11.3)	(41.6)	(3.5)	(5.4)	_	107.2
$K[Cu^{II}(I^{1})]$	Green	811 0 42	219_223*	11.5)	41.0)	34	57	_	110.1
Red (E)]	Green	01.1, 0.12	215 225	(12.1)	(41.2)	(3.4)	(53)		110.1
$K[Zn^{II}(L^1)]$	White	662 034	288-295*	12.2	40.9	41	51	_	115.4
(L)		0012, 010 1	200 200	(12.4)	(41.1)	(3.4)	(5.3)		
$K[Cd^{II}(L^1)]$	White	68.3. 0.38	203-208*	20.1	38.0.9	3.0	5.3	_	116.2
				(19.6)	(37.7)	(3.1)	(4.9)		
$K[Hg^{II}(L^1)]$	White	73.2, 0.47	253-257*	30.8	32.9	2.7	4.3	-	106.8
· · ·				(30.3)	(32.7)	(2.7)	(4.2)		
W2	Pale vellow	84, 0.61	Oilv	_	45.6	8.4	10.2		_
	raie yenow	0 1, 0101	ony		(45.1)	(8.3)	(10.5)	_	
H_3L^2	Yellow	73, 5.8	156-158	-	40.3	7.5	7.7	-	_
-					(40.4)	(7.1)	(7.8)	-	
$K_2[Cr^{III}(L^2)Cl_2]$	Blue	73, 0.39	277-279	9.2	26.3	4.4	4.8	13.1	149.1
				(9.4)	(26.0)	(4.0)	(5.0)	(12.8)	
$K_3[Mn^{II}(L^2)Cl_2]$	Red-brown	82, 0.48	281-286*	9.4	23.8	4.3	5.1	11.6	247.9
				(9.2)	(24.1)	(3.7)	(4.7)	(11.9)	
$K_3[Fe^{II}(L^2)Cl_2]$	Red	58, 0.29	210-213	9.2	24.21	4.2	4.3	12.4	210.5
				(9.3)	(24.1)	(3.7)	(4.7)	(11.9)	
$K[Co^{II}(L^2)]$	Brown	64, 0.28	>320	13.3	31.6	5.1	6.1	-	98.6
141 Y 11/1 2 1	6	04 0 05	100 100	(13.0)	(31.9)	(4.9)	(6.2)		110.0
$K[NI''(L^2)]$	Green	81, 0.35	180-183	13.1	31./	5.2	6.1	-	118.2
$W[C_{1}]/(1^{2})$	Casea	CC 0.20	257 200*	(13.0)	(31.9)	(4.9)	(6.2)		100.1
$K[Cu^{-}(L^{-})]$	Green	66, 0.29	257-260	13.6	31.9	4.4	5.8	-	100.1
$V[7\mathbf{p}^{ll}(1^2)]$	White	60.026	201 204*	(13.9)	(31.6)	(4.8)	(6.1)		105.4
K[ZII (L)]	vvince	00, 0.20	201-204	(14.4)	30.9 (31.4)	5.Z (4.8)	5.9 (6.1)	-	103.4
$K[Cd^{II}(I^2)]$	Pale vellow	63 0 31	181_187*	217	27.9	50	53	_	106.2
	r uic ychow	03, 0.31	101-107	(22.2)	(28.5)	(46)	(5.5)		100.2
$K[Hg^{II}(L^2)]$	White	70.2, 0.40	300-303*	33.1	24.9	4.0	5.1	_	116
		, , , , , , , , , , , , , , , , , , , ,		(33.8)	(24.3)	(3.7)	(4.7)		
				(· · · · /	· · · · /	··· /			

(*) = Decomposed.



Scheme 3. The *cis* I and *trans* II forms of precursors exist in the solid state and in solution.

the thiolate group [29]. The IR spectra of the complexes exhibited H_3L^1 and H_3L^2 bands with the appropriate shifts due to complex formation (Table 2). The absence of a peak around 2545–2619 cm⁻¹ in all the complexes indicates the deprotonation of (S–H) group upon complex formation. The v(C=0) amide vibration at 1660–1645 cm⁻¹ in the free ligands is shifted and observed around 1600–1650 and 1597–1640 cm⁻¹ for the H_3L^1 and H_3L^2 complexes, respectively indicating coordination of the nitrogen of the amide group to the metal atoms [30,31]. The v(C=S) stretching

round 1029–1035 cm⁻¹ in the the H_3L^1 and H_3L^2 is shifted to higher frequency and observed around 1040–1060 and 1036–1081 cm⁻¹ for H_3L^1 and H_3L^2 complexes, respectively indicating coordination of sulfur atom of the C–S moiety to the metal atoms [32]. At lower frequency the complexes exhibited bands around 453–583 and 366–398 cm⁻¹ which are assigned to the v(M-N) and v(M-S) vibration modes, respectively [32,33]. The IR spectra of the complexes $K_2[Cr^{III}(L^n)Cl_2]$ and $K_3[M'^{II}(L^n)Cl_2]$ (M' = Mn(II) or Fe(II); n = 1 or 2) exhibit far-IR active bands around 283–301 cm⁻¹ which are assigned to the v(M-CI) vibrations. These vibrations are characteristic of terminally coordinated chloride [32,34,35].

4.2. NMR spectra

The ¹H and ¹³C NMR spectra of W1, W2 and the Mannich bases H_3L^1 and H_3L^2 displayed signals corresponding to the various proton and carbon nuclei consistent with the proposed structural formula (Section 3). In solution, as in solid state, W1, W2 can exist in two conformation forms; the *cis* form I and the *trans* form II (Scheme 3). In the NMR spectra (DMSO-d₆ solution), for both





Scheme 5. Intermolecular hydrogen bonding interaction formed in the solid state.

precursors, we observed the presence of double signals for the protons, as well as double signals for carbons of both compounds. Signals at 148.4 (C₂, C=O; *cis* isomer), 166.7 (C₂, C=O; *trans* isomer) and 168.5 (C₂, C=O; *cis* isomer), 172.2 (C₂, C=O; *trans* isomer) were observed for W1 and W2, respectively. This is perhaps due to the fact that the rotational isomers of thioacetamide were sufficiently slow on the NMR time scale to allow the detection of the trans and cis isomers by NMR spectroscopy [36]. The NMR spectra for $K[Zn(L^1)]$ and $K[Zn(L^2)]$ complexes in DMSO-d₆ are examined in comparison with those of the parent Mannich bases H_3L^1 and H_3L^2 . In the ¹H NMR spectra of complexes, a signal assignable to thiol group protons at ca. 2.6 ppm in the free ligands was absent, indicating that deprotonation of thiol group occurred and that coordination through this group took place. Upon complexation

pletely disappeared in the spectra of their Zn(II) complexes indicat-
ing that the POH proton is removed and replaced by the potassium
ion. This has been supported by the chemical analysis and the
molar conductivity measurements of the complexes, indicating
the ligands behave as a tribasic molecule upon complex formation
Upon Zn(II) coordination, the protons PCH ₂ N are shifted downfield
indicating the coordination of the nitrogen atoms to the metal cen-
tre, because the deshielding effect of the metal centre. The protons
assigned due to the $C_{4,4';8,8'}$ -H and $C_{3,3'}$ -H in the H_3L^1 and H_3L^2
respectively were found at around δ 7.2 and 3.3 ppm in the spectra
of the free ligands. These protons undergo downfield shift in the
zinc complexes indicating participation of the nitrogen atoms
attached to these groups in coordination with the metal ions. Thus
the ¹ H NMR results support the modes of coordination suggested
by IR data. Upon complexation, the ³¹ P{ ¹ H} signal is shifted down-
field by ca. 24 ppm because the deshielding effect of the metal
centre.

4.3. Mass spectra

The mass spectra of the ligands and precursors were also consistent with the proposed structural formulae (see Section 2). The

IR frequencies (cm ⁻¹) o	f the compounds.
Compound	w(C-0)

Table 2

Compound	v(C==0)	v(P=O)	v(C-S)	v(P–C)	v(M-N)	v(M-S)	v(M–Cl)
H_3L^1	1660	1178	1029	1442			
$K_2[Cr^{III}(L^1)Cl_2]$	1620	1140	1045	1330	583	385	287
$K_3[Mn^{II}(L^1)Cl_2]$	1610	1160	1040	1327	563	388	291
$K_3[Fe^{II}(L^1) Cl_2]$	1645	1133	1042	1350	466	376	301
$K[Co^{II}(L^1)]$	1617	1140	1044	1333	453	389	-
$K[Ni^{II}(L^1)]$	1605	1120	1060	1350	459	366	-
$K[Cu^{II}(L^1)]$	1600	1140	1039	1373	516	390	-
$K[Zn^{II}(L^1)]$	1608	1160	1055	1370	505	388	-
$K[Cd^{II}(L^1)]$	1621	1159	1045	1326	510	391	-
$K[Hg^{II}(L^1)]$	1650	1175	1040	1380	560	398	
H_3L^2	1645	1180	1035	1440	-	-	-
$K_2[Cr^{III}(L^2)Cl_2]$	1599	1139	1036	1400	550	385	283
$K_3[Mn^{II}(L^2)Cl_2]$	1601	1165	1081	1388	530	388	288
$K_3[Fe^{II}(L^2) Cl_2]$	1616	1110	1080	1400	466	376	299
$K[Co^{II}(L^2)]$	1607	1155	1058	1391	453	389	-
$K[Ni^{II}(L^2)]$	1597	1130	1068	1388	459	366	-
$K[Cu^{II}(L^2)]$	1611	1154	1039	1397	516	390	-
$K[Zn^{II}(L^2)]$	1621	1155	1038	1396	495	385	-
$K[Cd^{II}(L^2)]$	1626	1158	1041	1390	511	391	-
$K[Hg^{II}(L^2)]$	1640	1170	1037	1401	542	389	

Table 3

Magnetic moment and UV-	is spectral data in DMF solutions.
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Compound	$\mu_{ m eff}$ (BM) (per atom)	Band position (λ , nm)	Extinction coefficient ε_{max} (dm ³ mol ⁻¹ cm ⁻¹)	Assignments
$K_2[Cr^{III}(L^1)Cl_2]$	3.81	317	573	$\pi ightarrow \pi^*$
21. (). 21		370	203	СТ
		425	300	${}^{4}A_{2}g^{(F)} \rightarrow {}^{4}T_{1}g^{(F)}(v_{2})$
		675	40	${}^{4}A_{2}g^{(F)} \rightarrow {}^{4}T_{2}g^{(F)}(v_{1}) (10Dq)$
		820	18	$({}^{4}A_{2}\sigma \rightarrow {}^{2}T_{1}\sigma {}^{2}F\sigma^{(G)})$
K ₂ [Mn ^{II} (L ¹)Cl ₂]	5 38	320	830	$\pi \rightarrow \pi^*$
Rafinin (E.)eizj	5.50	465	130	${}^{6}A_{1}\sigma \rightarrow {}^{4}T_{2}\sigma^{(G)}$
		690	88	$^{6}A_{1}\sigma \rightarrow {}^{4}T_{1}\sigma^{(G)}$
K[Fe ^{ll} (I ¹)]	4.25	319	890	$\pi \rightarrow \pi^*$
Refer (E)]	1.25	469	205	${}^{5}A_{0}\sigma \rightarrow T_{0}\sigma$
		670	100	$^{5}T_{0}\sigma \rightarrow ^{5}F\sigma$
$K[Co^{II}(I^{1})]$	3 88	307	527	125 - 25
K[CU(L)]	5.88	368	850	$n \rightarrow n$
		540	105	$4_{\Lambda_{-}\sigma}(F)$, $4_{T_{-}\sigma}(F)$
		672	105	$A_{2}g^{(F)} \rightarrow I_{2}g^{(F)}$ $4\Lambda g^{(F)} \rightarrow 4T g^{(F)}$
KINGH(11)	Diamagnotic	242	790	$\pi_{2g} \rightarrow \pi_{1g}$
	Diamagnetic	270	1100	$n \rightarrow n$
		404	149	$1 \Lambda \alpha = 1 P \alpha$
		404	148	$A_1g \rightarrow D_1g$
	1.02	282	4/	$A_1g \rightarrow A_2g$
K[CU (L)]	1.82	333	1050	$\pi \to \pi$
		353	810	CI 20
		671	95	$^{-B_1}g \rightarrow ^{-B_2}g$
Mar Her 151		815	/5	$^{2}B_{1}g \rightarrow ^{2}A_{2}g$
K[Zn''(L')]	Diamagnetic	314	1000	$\pi ightarrow \pi^*$
recoller 155		334	570	CI
K[Cd''(L')]	Diamagnetic	320	1500	$\pi ightarrow \pi^*$
THE LET 1 Y		366	300	CI
K[Hg"(L')]	Diamagnetic	282	1920	$\pi \rightarrow \pi^*$
		351	400	CI
$K_3[Cr^m(L^2)Cl_2]$	3.83	299	850	$\pi ightarrow \pi^*$
		370	750	
		440	250	${}^{4}A_{2}g^{(r)} \rightarrow {}^{4}T_{1}g^{(r)}(v_{2})$
		746	20	${}^{4}A_{2}g^{(r)} \rightarrow {}^{4}T_{2}g^{(r)}(v_{1}) (10Dq)$
$K_2[Mn^n(L^2)Cl_2]$	5.36	310	690	$\pi \rightarrow \pi^*$
		440	110	${}^{6}A_{1}g \rightarrow {}^{4}T_{2}g^{(G)}$
		560	33	${}^{6}A_{1}g \rightarrow {}^{4}T_{1}g^{(G)}$
$K[Fe^{II}(L^2)]$	4.25	302	1010	$\pi ightarrow \pi^*$
		360	615	CT
		590	90	${}^{5}T_{2}g \rightarrow {}^{5}Eg$
$K[Co^{II}(L^2)]$	3.81	288	527	$\pi ightarrow \pi^*$
		313	344	CT
		409	87	${}^{4}A_{2}g^{(F)} \rightarrow {}^{4}T_{2}g^{(F)}$
		603	110	${}^{4}A_{2}g^{(F)} \rightarrow {}^{4}T_{1}g^{(F)}$
$K[Ni^{II}(L^2)]$	Diamagnetic	275	551	$\pi ightarrow \pi^*$
		348	228	CT
		404	148	$^{1}A_{1}g \rightarrow {^{1}B_{1}g}$
		633	47	$^{1}A_{1}g \rightarrow ^{1}A_{2}g$
K[Cu ^{II} (L ²)]	1.80	319	415	$\pi ightarrow \pi^*$
		580	58	${}^{2}B_{1}g \rightarrow {}^{2}B_{2}g$
		815	15	$^{2}B_{1}g \rightarrow ^{2}A_{2}g$
$K[Zn^{II}(L^2)]$	Diamagnetic	304	720	$\pi ightarrow \pi^*$
		374	385	СТ
$K[Cd^{II}(L^2)]$	Diamagnetic	295	790	$\pi ightarrow \pi^{*}$
		366	310	CT
$K[Hg^{II}(L^2)]$	Diamagnetic	299	790	$\pi ightarrow \pi^*$
		356	300	СТ

positive ion FAB mass spectra for $K_3[Fe(L^1)Cl_2]$, $K[Ni(L^1)]$, $K_3[Fe(L^2)Cl_2]$, $K[Zn(L^2)]$ and $K[Hg(L^2)]$ complexes were reported. The mass spectrum of $K_3[Fe(L^1)Cl_2]$ showed several peaks corresponding to successive fragmentation of the molecule. The first peak observed at m/z 665.63 (7.57%) represents the molecular ion peak of the complex. Other distinct peaks were observed in the mass spectrum at m/z 627.5, 118 and 56 can be assigned to the (M–K)⁺, (CH₃FeCH₂SH)⁺, fragments and the final metal residue (Fe). The spectrum of K[Ni(L¹)] showed several peaks in the mass spectrum at m/z 481.3, 156 and 58 assigned to the (M–K)⁺, (HOP(O)NiSH)⁺ fragments of the complex and the metal residue, respectively. These results are similar to those of analogous complexes reported earlier by others [32,33]. The mass spectrum of $K_3[Fe(L^2)Cl_2]$ showed the molecular ion peaks at m/z 449. Other

peaks at m/z 367, 296 and 56 assigned to $[M-{(K)+(H_2C=CH-CH_3)}]^+$, $[M-{(K)+(H_2C=CH-CH_3)+(HNCOCH_2)}]^+$ and (Fe) residue, respectively. The mass spectrum of K[Zn(L²)] showed peaks at m/z 418.03, 87 and 65 assigned to $(M-K)^+$, ZnS and metal residue, respectively. The mass spectrum of K[Hg(L²)] showed peaks at m/z 555.19, 504.38, 312.81 and 243 assigned to $[M-(K+H)]^+$, $[M-(K+CH_2SH)+(HOPOHg)]^+$ and HgS, respectively.

4.4. Electronic spectra and magnetic moments measurements

The UV–Vis spectrum of H_3L^1 exhibits an intense absorption peak at 299 nm, assigned to $\pi \rightarrow \pi^*$. A very low intensity peak at 320 nm in H_3L^1 spectrum was attributed to the $n \rightarrow \pi^*$ transition.

Table 4L:M mole ratio of some metal complexes at λ_{max} nm in DMF solutions.

Complexes	λ_{\max} (nm)	L:M ratio
$K_2[Cr^{III}(L^1)Cl_2]$	425	1:1
$K_3[Fe^{II}(L^1)Cl_2]$	469	1:1
$K[Zn^{II}(L^1)]$	334	1:1
$K[Hg^{II}(L^1)]$	351	1:1
$K_2[Cr^{III}(L^2)Cl_2]$	440	1:1
K[Ni ^{II} (L ²)]	404	1:1
$K[Zn^{II}(L^2)]$	374	1:1

The spectrum of H_3L^2 exhibits a similar intense absorption at 312 nm, and the expected $n \rightarrow \pi^*$ transition is hidden by this band. The electronic spectra of the complexes of H₃L¹ exhibited various extents of bathochromic shift of the bands related to the intraligand $\pi \to \pi^*$ transition, except for that of the Hg(II) complex which showed a hypsochromic shift (see Table 3). Bands related to the (CT) transitions were observed in the spectra of the 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 ${}^{4}A_{2}g^{(F)} \rightarrow {}^{4}T_{1}g^{(F)}$ (v₂), ${}^{4}A_{2}g^{(F)} \rightarrow {}^{4}T_{2}g^{(F)}$ (v₁)(10 Dq) and ${}^{4}A_{2}g \rightarrow {}^{2}T_{1}g$, ${}^{2}Eg^{(G)}$ [37–39]. The band related to the v_3 may be located at higher wave number and hidden by the (CT) or ligand band [26]. The magnetic behaviour of octahedral Cr(III) is independent of the field strength of the ligand. It is expected that the magnetic moment for Cr(III) complexes should be approximately equal to the calculated spin value only. The Cr(III) complex under consideration has the value of 3.81 BM, which matches. Thus, the ligand field bands, magnetic moment value, molar conductance as well as the other analytical data support an octahedral geometry [32,40]. The electronic spectra of the Mn(II) complex presents a signal in the UV region at 320 nm assigned to ligand field and/or a transfer of electric load, according with the theory data for a d⁵ ion. Mn-complex shows two spin forbidden transition bands at 465 and 690 nm, which may be assigned to ${}^{6}A_{1}g \rightarrow {}^{4}T_{2}g^{(G)}$ and ${}^{6}A_{1}g \rightarrow {}^{4}T_{1}g^{(G)}$ respectively, indicating a distorted octahedral geometry for the complex. The magnetic moment of this complex is typical for a high spin octahedral structure. The Fe(II) complex showed the $\pi \rightarrow \pi^*$ and d–d bands which could be attributed to spin forbidden transition in a distorted octahedral geometry [37,39,40]. The observed magnetic moment of 4.25 BM is consistent with a high spin octahedral structure. For the Co(II) complex, there are 2 orbital forbidden absorptions bands at 603 and 408 nm are observed. These were assigned to ${}^{4}A_{2}g^{(F)} \rightarrow {}^{4}T_{2}g^{(F)}$ and ${}^{4}A_{2}g^{(F)} \rightarrow {}^{4}T_{1}g^{(F)}$ transitions, respectively. The

electronic spectrum of the Co(II) complex is consistent with tetrahedral assignment [41]. The observed room temperature magnetic moment value is 3.88 BM, which supports a high-spin tetrahedral structure for the Co(II) ion with the ${}^{4}A_{2}$ ground state. The slightly lower magnetic moment might be due the slight deviation from the regular tetrahedral geometry. The electronic spectrum of the Ni(II) complex displayed two d-d transitions at 404 and 585 nm. The molar conductance value, in DMF at 107.2 $\mbox{cm}^2\,\Omega^{-1}\,\mbox{mol}^{-1}$ indicated that the complex is a 1:1 electrolyte, and other analytical data supported the formation of four coordinate Ni-complex. Based on the diamagnetic behaviour of the Ni(II) complex the four coordinate Ni(II) complex is consistent with a square planar geometry [42]. The magnetic moment value of the green Cu(II) complex, as well as the other analytical data, are in agreement with square planar structures [37,43–45]. The Cu(II) complex gave brown colour in DMF solution indicating further coordination to solvent molecules. Thus, the spectrum of the Cu(II) complex in DMF exhibited two low intensity bands which are characteristic of distorted octahedral Cu(II) complexes. The spectra of the Zn(II), Cd(II) and Hg(II) complexes exhibited bands assigned to ligand $\pi \rightarrow \pi^*$ and $L \rightarrow M$ charge transfer [37]. These complexes are diamagnetic as expected. Based on molar conductance values of the complexes in DMF 106–115 cm² Ω^{-1} mol⁻¹ as well as the other analytical data, we proposed tetrahedral coordination for these three complexes. This assignment is in analogy with those described for Zn(II), Cd(II) and Hg(II) complexes containing N_2S_2 system [32,31]. The electronic spectra of the complexes of H_3L^2 exhibited bands related to the intra-ligand $\pi \rightarrow \pi^*$ and the (CT) transitions (see Table 3). The spectra of the Cr(III), Mn(II), Fe(II) and Cu(II) complexes of H₃L² showed similar behaviour to those of H₃L¹ suggesting octahedral geometries for the complexes in solutions. As for $K[Co(L^1)]$ the spectrum of Co(II) complex of H_3L^2 together with the μ_{eff} values (Table 3) suggests tetrahedral geometry [32,37,41]. The spectrum of the Ni(II) complex displayed bands characteristic of square planar geometry [37,42]. The magnetic moment value was consistent with the square planar structure. The spectra of Zn(II), Cd(II) and Hg(II) complexes of H_3L^2 showed similar behaviour to those of $H_{2}L^{1}$ suggesting tetrahedral geometries [37].

5. Molar ratio

Complex formation by molar ratio of ligand to metal ion was also studied in DMF solution. A series of solutions containing constant concentration of metal ion $(1 \times 10^{-3} \text{ M})$ were treated with



Fig. 1. Plot represents mole ratio; absorbance of solution at λ_{max} vs. [L]/[M] for some complexes.

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 λ_{max} of the complexes against [L]/[M], Table 4 and Fig. 1, which showed a 1:1 M:L ratio for the complexes. These data are in agreement with those observed for the solid state.

6. Conclusion

In this paper, we have explored the synthesis and coordination chemistry of some monomeric complexes obtained from the reaction of the polydentate N_2S_2 Mannich base ligands H_3L^1 and H_3L^2 with some metal ions. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. Upon complex formation, the ligands provide the appropriate arrangement around metal centre allowing the metal to achieve its preferred geometry. The metals follow similar patterns, adding chlorides when a preference of octahedral geometries is required. 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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