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Ligational behaviour of (E)-2-amino-N'-[1-(2-hydroxyphenyl) ethylidene]benzohydrazide towards later 3d metal ions: X-ray crystal structure of nickel(IV) complex



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HIGHLIGHTS

• Hydrazone ligand (Aheb) and its metal complexes were synthesized and characterized.

• Oxidation of Ni(II) to Ni(IV).

• Comparative study of crystal structure of ligand and its Ni(IV)complex.

G R A P H I C A L A B S T R A C T



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ABSTRACT

Ligational behaviour of (*E*)-2-amino-N'-[1-(2-hydroxyphenyl)ethylidene]benzohydrazide (Aheb) towards later 3d metal ions[copper(II), cobalt(II), manganese(II), zinc(II), cadmium(II) and nickel(IV)] has been studied. Their structures have been elucidated on the basis of spectral (IR, ¹H NMR, UV–Vis, EPR and FAB-mass), elemental analyses, conductance measurements, magnetic moments, and thermal studies. During complexation Ni(II) ion has got oxidized to Ni(IV). The changes in the bond parameters of the ligand on complexation has been discussed by comparing the crystal structure of the ligand with that of its Ni(IV) complex. The X-ray single crystal analysis of [Ni(aheb)₂]Cl₂·4H₂O has confirmed an octahedral geometry around the metal ion. EPR spectra of the Cu(II) complex in polycrystalline state at room (300 K) and liquid nitrogen temperature (77 K) were recorded and their salient features are reported. © 2014 Elsevier B.V. All rights reserved.

1. Introduction

Hydrazones merit special attention due to their varied structural features. The possibility of tautomerism in this class of compounds has drawn additional attraction. In addition, hydrazones constitute an important class of compounds for new drug development and

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catalysis as well. The active pharmacophore (NH—N=CH—) of hydrazones is mainly responsible for the significant biological activities. Some of the more effective anti-tuberculosis drugs like isoniazide, isocarboxazide and iproniazide [1], antinociceptive/ antiinflammatory agent like Safrole [2], anti-platelet agent like benzylidene 10*H*-phenothiazine-1-carbohydrazide [3] contain hydrazide/hydrazone moiety. Besides being biologically active, metal complexes of hydrazones play an important role in catalysis [4–7].

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Encouraged by these reports and in continuation of our studies on the synthesis and characterization of hydrazones and their ligational behaviour towards late 3d metal ions [8,9], we undertook the study of transition metal complexes of (*E*)-2-amino-*N*'-[1-(2hydroxyphenyl)ethylidene]benzohydrazide (Aheb) containing >C=O, >C=N— and —OH groups as potential coordinating sites. On complexation, ligand (Aheb) act as a tridentate ligand, coordinating through carbonyl oxygen, azomethine nitrogen and phenolic oxygen via deprotonation. During complexation Ni(II) ion has got oxidized to Ni(IV) as evidenced by single crystal X-ray analysis and magnetic moment value.

2. Experimental

2.1. Materials and methods

All the solvents used in the present investigation are of analytical grade and were used without further purification. Methyl anthranilate, hydrazine hydrate, o-hydroxyacetophenone, and hydrated metal salts were obtained from S.D. Fine chemical company, India. 2-Aminobenzoylhydrazide was prepared by known method [10]. The metal content of the complexes was determined volumetrically using EDTA after decomposition with a mixture of HCl and HClO₄. The chloride content of the complexes was determined gravimetrically as AgCl. The carbon, hydrogen and nitrogen contents in each sample were determined using Heraus C H N rapid analyzer. IR spectra in the 4000–400 cm⁻¹ range were measured on Thermo Nicolet 320 FT-IR spectrometer using KBr discs. ¹H NMR spectra were recorded in DMSO-*d*₆ as the solvent at 400 MHz on a BRUKER AMX 400 spectrometer using tetramethylsilane (TMS) as an internal reference. Electronic spectra of the complexes were recorded on a Varian CARY 50 Bio UV-Visible spectrometer. EI mass spectrum was recorded on a M.I Ver. 14 on UIC 002002. FAB mass spectrum of the complex was recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using

Argon/Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and spectra were recorded at room temperature. The magnetic susceptibility measurements were carried out on a Faraday balance using Hg[Co(NCS)₄] as the calibrant and diamagnetic corrections were made by direct weighing of the ligand for diamagnetic pull. Conductance measurements were recorded in DMSO using Elico conductivity bridge type CM-82, provided with a dip type conductivity cell fitted with platinum electrodes. EPR spectra were recorded on Varian E-4 X-band spectrometer using tetracyanoethylene (TCNE) as 'g' (g = 2.0027) marker at room temperature and also at liquid nitrogen temperature. Thermal stabilities of the complexes were studied in the temperature range 25-1000 °C using a TGA7 analyzer, Perkin Elmer at a heating rate of 10 °C per min in a N₂ atmosphere. A suitable crystal of the Ni(IV) complex was mounted on a Bruker SMART APEX II CCD diffractometer. Reflection data were measured at 293(2) K using Mo K α radiation $(\lambda = 0.71073 \text{ Å})$ with a graphite monochromator empirical absorption correction was carried out by using SADABS program [11]. The structure of the complex was solved by heavy atom method and refined by least square on F^2 using the SHELX-97 software package [12]. All non H atoms were anisotropically refined. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms. The final conventional R(F) = 0.0672and $wR(F^2) = 0.1519$ for $I > 2\sigma(I)$ with weighting scheme, $w = 1/2\sigma(I)$ $[\sigma^2(F^2) + (0.0848P + 0.0000P], \text{ where } P = (F^2 + 2Fc^2)/3.$

2.2. Synthesis

2.2.1. Synthesis of the (E)-2-amino-N'-(1-(2-hydroxyphenyl) ethylidene)benzohydrazide ligand

The (*E*)-2-amino-*N*'-[1-(2-hydroxyphenyl)ethylidene]benzohydrazide was prepared according the literature method [13] with a slight modification: A mixture of *o*-aminobenzoylhydrazide (7.60 g; 50.33 mmol) and *o*-hydroxyacetophenone (6.80 g; 50 mmol) in ethanol (25 cm³) was stirred (Scheme 1) for 2 h at room temperature.

(a) Refluxed in ethanol for 2 h (b) hydrated metal chlorides, ethanol, sodium acetate

Scheme 1. Synthesis of (*E*)-2-amino-*N'*-[1-(2-hydroxyphenyl)ethylidene]benzohydrazide ligand and its metal complexes, M = copper(II), cobalt(II), manganese(II), zinc(II) cadmium(II) [*X* = Nill, *Y* = 3] and nickel(IV) [*X* = 2CI, *Y* = 4].



The resulting yellowish compound that precipitated was filtered, washed and recrystallised from ethanol.

Yield 80%, M.P.:170–171 °C (literature reported: 170 °C).

2.2.2. Synthesis of the transition metal complexes

Metal(II) chlorides (1 mmol) were treated with Aheb (0.02 mmol; 0.5386 g) in 1:2 ratio in alcoholic medium and refluxed for about 2 h. Sodium acetate (2 g) was added to the reaction mixture and refluxing was continued for another hour (Scheme 1). The complexes precipitated were filtered, washed with alcohol and finally air dried. All the isolated complexes are insoluble in most of the organic solvents but soluble in DMF and DMSO.

Yield: 85–90%.

3. Results and discussion

3.1. General characterization

The analytical data along with some physical properties of the complexes are summarized in Table 1. The elemental analyses show 1:2 (metal:ligand) stoichiometry for all the complexes. The complexes can be represented by the formulae [M(aheb)₂]·3H₂O for copper(II), cobalt(II), manganese(II), zinc(II), and cadmium(II) complexes and [Ni(aheb)₂]Cl₂·4H₂O for nickel(IV) complex. The observed molar conductance values indicate its 1:2 electrolytic nature for Ni(IV) complex while non-electrolytic nature for copper(II), cobalt(II), zinc(II), and cadmium(II) cobalt(II), manganese(II), zinc(II), and cadmium(II) complexes.

3.2. Crystallographic study of Ni(IV) complex

The crystal structure consists of a discrete $[Ni(aheb)_2]^{2+}$ cation and two uncoordinated chloride anions and four water molecules. The ORTEP view of the complex with atom labelling is shown in Fig. 1a. The experimental crystallographic details are given in Table 2. The selected bond lengths and angles, torsional angles, hydrogen bonds and equations for the main least square planes in the structure are given in Tables 3–5 respectively. The coordination geometry of the Ni(IV) can be described as a distorted octahedral geometry. The Ni(IV) ion is bonded to two carbonyl oxygens [O(2) and O(4)], two azomethine nitrogens [N(1) and N(4)] and two deprotonated phenolic oxygens [O(2), O(4), O(1) and O(3)] occupy the equatorial belt and two nitrogen atoms [N(1) and N(4)] occupy the axial position of the octahedron.

The angles O(3)—Ni(1)—O(2), O(1)—Ni(1)—O(4), O(4)—Ni(1)—O (2) and O(1)—Ni(1)—O(3) measures 91.58(13), 91.94(13), 79.91 (12) and 101.23(13)°, respectively which deviates from a perfect octahedral geometry (90°). The [N(1)—Ni(1)—N(4)] angle measures 166.76(12)° and deviates from 180° expected for a perfect octahedral geometry. The C—C—C bond angles in aromatic rings are around 120° with the variation being less than 3°, tallying closely with sp²-hybridized carbons. The conformational designa-



Fig. 1a. ORTEP diagram of [Ni(aheb)₂]Cl₂·4H₂O.

tions across the bonds C(9)-C(10)-C(11)-N(3), O(2)-C(9)-C(10)-C(11), C(24)-C(25)-C(30)-N(6) and O(4)-C(24)-C(25)-C(30) indicate the *+synperiplanar* arrangement and their torsional angles are +5.8(7), +9.1(6), +4.3(7) and +10.4(6)° respectively.

The C—C bond distances in aromatic rings are in the normal range of 1.35–1.49 Å, which are characteristic of delocalised aromatic rings. The bond distances Ni(1)—N(4) 2.045(3), Ni(1)—N(1) 2.049(3), Ni(1)—O(1) 2.062(3), Ni(1)—O(3) 2.067(4), Ni(1)—O(4) 2.080(3) and Ni(1)—O(2) 2.092(3) Å are in good agreement with the bond distances found in similar distorted octahedral Ni(IV) complexes [14–16]. The bond distances for the bonds O(4)—C(24), O(2)—C(9), O(3)—C(16), O(1)—C(1), N(3)—C(11), and N(6)—C(30) are 1.254(5), 1.257(5), 1.451(5), 1.445(5), 1.357(6) and 1.350(6) Å respectively. The bond distances N(1)—C(7) 1.278(5) and N(4)—C(22) 1.286(5) Å are indicative of double bonds.

The Ni(IV) complex is coplanar and lies in five planes with plane I [C(1), C(2), C(3), C(4), C(5), C(6)] forms a dihedral angle of $4.39(1)^{\circ}$ with plane II [C(16), C(17), C(18), C(19), C(20), C(21)], 56.23(1)^{\circ} with plane III [C(25), C(26), C(27), C(28), C(29), C(30)], 55.58(1)^{\circ} with plane IV [C(10), C(11), C(12), C(13), C(14), C(15)], 70.99(1)^{\circ} with plane V [O(1), O(2), O(3), O(4), Ni(1)]. Plane II form dihedral angles 55. $54(1)^{\circ}$, $56.04(1)^{\circ}$, $71.11(1)^{\circ}$ with planes III, IV and V respectively. Plane III forms a dihedral angle of $12.49(1)^{\circ}$, $53.60(1)^{\circ}$ with planes IV and V respectively. Further plane IV forms a dihedral angle of $53.60(1)^{\circ}$ with plane V.

The molecular packing diagrams of the [Ni(aheb)₂]Cl₂·4H₂O in the unit cell is illustrated in Fig. 1b. Molecular packing is mainly dictated by a three-dimensional hydrogen-bonding network

Table 1

	Analytical	and ph	iysicochemical	data of ah	ieb and i	its metal	complexe
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Compound	Empirical formula	Elemental analyses found (calculated) (%)					μ_{eff} (B.M.)	$\Lambda_M \ ^a$	$\lambda_{\rm max}$ in cm ⁻¹
		С	Н	Ν	М	Cl			
Aheb	$C_{15}H_{14}N_3O_2$	66.95 (66.90)	5.59 (5.61)	15.55 (15.58)	-	-	-	-	27777
[Cu(aheb)2]·3H2O	$[Cu(C_{15}H_{14}N_{3}O_{2})_{2}]\cdot 3H_{2}O$	55.00 (55.08)	5.25 (5.23)	12.85 (12.84)	9.70 (9.71)	-	1.79	10.08	28169, 14705
[Co(aheb) ₂]·3H ₂ O	[Co(C ₁₅ H ₁₄ N ₃ O ₂) ₂]·3H ₂ O	55.45 (55.47)	5.20 (5.27)	12.95 (12.93)	9.00 (9.07)	-	4.85	9.57	14513, 18832
[Ni(aheb) ₂]Cl ₂ ·4H ₂ O	[Ni(C ₁₅ H ₁₄ N ₃ O ₂) ₂]Cl ₂ ·4H ₂ O	48.79 (48.80)	4.89 (4.91)	11.37 (11.38)	7.92 (7.94)	9.59 (9.60)		12.75	28571
[Mn(aheb) ₂]·3H ₂ O	$[Mn(C_{15}H_{14}N_{3}O_{2})_{2}]\cdot 3H_{2}O$	55.78 (55.81)	5.29 (5.30)	13.00 (13.01)	8.55 (8.50)		5.75	11.73	28409
[Zn(aheb)2]-3H20	$[Zn(C_{15}H_{14}N_{3}O_{2})_{2}]\cdot 3H_{2}O$	54.90 (54.92)	5.20 (5.22)	12.80 (12.81)	9.95 (9.96)	-	Dia	14.55	28985
[Cd(aheb) ₂]·3H ₂ O	$[Cd(C_{15}H_{14}N_3O_2)_2]\cdot 3H_2O$	51.22 (51.25)	4.85 (4.87)	11.90 (11.95)	15.95 (15.98)	-	Dia	13.56	347

^a Ω^{-1} cm² mol⁻¹.

Table 2

Crystal data and structural refinement for nickel(IV) complex.

Compound	$C_{30}H_{36}Cl_2N_6NiO_8$
CCDC no.	288644
Molecular weight	738.26
Colour/shape	Brownish black
Temp.	293(2) K
Crystal system	Triclinic
Space group	P-1
V	1692.1(11) Å ³
а	12.564(5) Å
b	13.201(5) Å
С	13.191(5) Å
α	61.508(5)°
β	65.938(5)°
γ	65.881(6)°
Ζ	2
D _{calcd}	1.449 mg m^{-3}
Index ranges	$-16\leqslant h\leqslant 16$
	$-17\leqslant k\leqslant 16$
	$-17 \leqslant l \leqslant 17$
F (000)	768
Absorption coefficient	0.788 mm^{-1}
Radiation	Μο Κα
Wavelength	0.71073 Å
Reflection collected	14149
Independent reflections	7569 $[R(int) = 0.1050]$
$T_{\rm max}$ and $T_{\rm min}$	0.8183, 0.7726
Crystal size	$0.34 \times 0.33 \times 0.27 \text{ mm}$
No. parameters	568
Goodness-of-fit (GOF)	0.963
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0672, wR_2 = 0.1519$
	$R_1 = 0.1195, wR_2 = 0.1747$
Largest diff. peak and hole	1.144, -0.491 e A ⁻³

involving cations, anions and water molecules. The complex shows intramolecular and intermolecular hydrogen bonding (Table 4). These hydrogen bonding stabilize the crystal-packing pattern.

 Table 3

 Selected bond lengths (Å) and angles along with the torsion angles (°) of Ni(IV) complex.

Table 4

Hydrogen bonds (Å) and angles (°) for nickel(IV) complex (symmetry transformations
used to generate equivalent atoms: (i) x, y, z and (ii) $x + 1/2$, $-y + 1/2 + 1$, $+z$.

D—H···A	D—H	H···A	D···A	<d—h···a< th=""></d—h···a<>
$\begin{array}{c} O(2) & -H(2)'' \cdots N(3)^i \\ N(1) & -H(1A) \cdots O(1)^i \\ N(2) & -H(2)' \cdots O(1)^{ii} \\ C(5) & -H(5) \cdots O(1)^{ii} \end{array}$	0.921(3)	1.731(3)	2.522(3)	142.09(2.42)
	0.798(3)	2.039(3)	2.664(3)	134.91(2.54)
	0.855(2)	2.063(2)	2.905(3)	168.24(2.13)
	0.963(2)	2.623(2)	3.320(3)	129.59(1.60)

Previously we reported the crystal structure of the (E)-2-amino-N'-(1-(2-hydroxyphenyl) ethylidene)benzohydrazide ligand [17]. The changes observed in the ligand on coordination are summarized as follows: The C=O [C(7)–O(1) bond length [1.241(2) Å] in ligand has increased in Ni(IV) complex [C(9)-O(2) 1.257(5) and C(24)–O(4) 1.254(5)Å] as a result of decrease in bond order upon complexation. The C=N [C(8)–N(3) 1.287 Å] bond distance in the ligand has decreased in Ni(IV) complex [C(7)–N(1) 1.278(2) and C(22)-N(4) 1.286(5)Å]. The reason for such a bond contraction may be attributed to electron delocalisation in the coordinated ligand [18]. On the other hand, the C–OH [C(14)–O(2)] bond distance which was 1.349(3) Å in the ligand has increased to [C(1)-O(1) 1.445(5) and C(16)-O(3) 1.451(5) Å] in Ni(IV)complex. In the ligand, the two planes C(1), C(2), C(3), C(4), C(5), C(6) and C(9), C(10), C(11), C(12), C(13), C(14) were almost planar with a deviation of $5.47(7)^{\circ}$, on complexation this deviation has increased. All the remaining bond lengths and bond angles do not show much change upon complexation.

3.3. Spectroscopic studies

The diagnostic IR bands of the ligand and the respective complexes are shown in Table 6. The bands at 3477 and 3365 cm⁻¹ in the infrared spectrum of the ligand may be assigned to the v_{as} (HNH) and v_{s} (HNH) vibrations of NH₂ groups and the band at

Bonds	Lengths	Bonds	Lengths
C(1)—N(1)	1.361(3)	C(8)—C(9)	1.475(3)
C(1)-C(2)	1.404(3)	C(8)-C(15)	1.492(3)
C(1)-C(6)	1.417(3)	C(9)—C(10)	1.399(3)
C(2)—C(3)	1.378(3)	C(9)—C(14)	1.410(3)
C(3) - C(4)	1.385(3)	C(10)-C(11)	1.376(4)
C(4) - C(5)	1.377(3	C(11)-C(12)	1.370(5)
C(5)—C(6)	1.396(3)	C(12)-C(13)	1.376(4)
C(6)—C(7)	1.484(3)	C(13)-C(14)	1.390(3)
C(7)—O(1)	1.241(2)	C(14)—O(2)	1.349(3)
C(7)—N(2)	1.361(2)	N(2)—N(3)	1.380(2)
C(8)—N(3)	1.287(2)		
Bonds	Angles	Bonds	Angles
N(1)-C(1)-C(2)	118.87(19)	N(3)-C(8)-C(15)	124.42(18)
N(1)-C(1)-C(6)	123.19(19)	C(9)—C(8)—C(15)	120.82(16)
C(2) - C(1) - C(6)	117.94(17)	C(10)-C(9)-C(14)	117.7(2)
C(3) - C(2) - C(1)	121.54(19	C(10)—C(9)—C(8)	120.37(18)
C(2) - C(3) - C(4)	120.5(2)	C(14)-C(9)-C(8)	121.91(17)
C(5)-C(4)-C(3)	118.8(2)	C(11)-C(10)-C(9)	121.2(3)
C(4) - C(5) - C(6)	122.24(17)	C(12)-C(11)-C(10)	120.4(3
C(5)-C(6)-C(1)	118.89(17)	C(11)-C(12)-C(13)	120.3(2)
C(5)-C(6)-C(7)	121.75(16)	C(12)-C(13)-C(14)	120.3(3)
C(1)-C(6)-C(7)	119.32(16)	O(2)-C(14)-C(13)	116.9(2)
O(1)-C(7)-N(2)	119.94(16)	O(2)-C(14)-C(9)	122.95(19)
O(1)-C(7)-C(6)	122.32(15)	C(13)-C(14)-C(9)	120.1(2)
N(2)-C(7)-C(6)	117.73(14)	C(7)–N(2)–N(3)	115.37(14)
N(3)-C(8)-C(9)	114.76(15)	C(8)—N(3)—N(2)	120.89(15)
Bonds	Torsion angles	Bonds	Torsion angles
N(1)-C(1)-C(6)-C(5)	179.08(19)	C(15)-C(8)-N(3)-N(2)	3.28(27)
C(5)-C(6)-C(7)-O(1)	161.12(18)	C(8) - C(9) - C(14) - O(2)	1.23(31)
O(1)-C(7)-N(2)-N(3)	5.56(25)		

Table 5 Least square planes through the mentioned atoms of Ni(IV) complex. Equation of the plane: m1x + m2y + m3z = D.

Planes	<i>m</i> 1	m2	<i>m</i> 3	D
I. C(9), C(10), C(11), C(12), C(13), C(14) II. C(1), C(2), C(3), C(4), C(5), C(6)	-0.76422 -0.77154	0.56545 0.50650	-0.31022 -0.38495	-1.91616 -2.28689
Plane-plane				Angle
Ι	II			5.47

Dihedral angles (°) formed by LSQ-planes.



Fig. 1b. Molecular packing diagram of $[Ni(aheb)_2]Cl_2\cdot 4H_2O$ (intra-and intermolecular hydrogen bonds are omitted for clarity).

3213 cm⁻¹ to v(NH) group of the ligand. In the spectra of all the metal complexes the bands of v_{as} (HNH) and v_{s} (HNH) vibrations of NH₂ were not observed and might have been obscured by the broad band at 3500 cm⁻¹, due to the lattice-held water molecules where as the band corresponding to v(NH) group remains the same as in the ligand [19,20]. Infrared spectrum of the ligand shows a broad weak band in the region 3052–2925 cm⁻¹ due to the intra-molecular hydrogen bonded OH with azomethine nitrogen moiety as also confirmed by crystallographic studies. The absence of this band in all the complexes, suggests the coordination of phenolic oxygen of the ligand to the metal via deprotonation as also confirmed by ¹H NMR spectra. The v(C–O) of phenolic moiety observed at 1292 cm⁻¹ in the ligand shows a positive shift of 10–40 cm⁻¹, confirming the involvement of deprotonated phenolic oxygen on complexation [21].

The bands at 1625, 1547 and 1257 cm⁻¹ are assigned to amide-I [vC=O], amide-II [v(CN) + δ (NH) and amide-III [δ (NH) + v(CN)]

vibrations respectively. The shift of the amide-I [v(C=O)] band to lower wave number compared to 2-aminobenzoylhydrazone of butane-2,3-dione [10] suggest the involvement of oxygen in hydrogen bonding which was also confirmed by crystallographic studies. A shift to lower frequency (10–20 cm⁻¹) of amide-I [v(C=O)] band in all the complexes is indicative of the coordinated C=O group. A shift to the lower wave number (10–40 cm⁻¹) in the amide II and to the slightly higher wave number (10–30 cm⁻¹) in the amide III bands in the complexes also confirm the C=O coordination [22]. The azomethine v(C=N) stretching observed at 1610 cm⁻¹ in the ligand spectrum has shifted to lower wave number (~1597–1585 cm⁻¹) in all the complexes, indicating coordination of azomethine nitrogen with the metal ions [23].

The numbering system followed for NMR assignments of ligand is given in Scheme 1. The chemical shift values δ (in ppm) are given in Table 7. The spectrum of the ligand exhibits three singlets at 13.43, 10.92 and 2.47 ppm, assignable to phenolic —OH group (D₂O exchangeable), NH (D₂O exchangeable) and methyl <u>p</u>rotons respectively. Two doublets at 6.80, 7.30 and two triplets at 7.24 and 6.61 ppm are assigned to aromatic protons C(2)H C(5)H and C(4)H, C(11)H respectively. A doublet expected of C(5)H and another doublet of C(10)H have merged to give a multiplet at 7.64 ppm, integrating for two protons. One triplet of C(12)H and another doublet of C(13)H have merged to give a multiplet at 6.61 ppm, which corresponds to two protons.

In the spectra of zinc(II), and cadmium(II) complexes, the resonance due to N(2)H has appeared at the same position as in the ligand (10.92 ppm) indicating the non-involvement of N(2)H in coordination. The singlet at 13.43 ppm in the ligand spectrum ascribed to phenolic —OH group is not observed in zinc(II), and cadmium(II) complexes. This confirms the involvement of phenolic oxygen in coordination with the metal via deprotonation. The other signals [C(15)H, C(2)H, C(5)H, C(4)H, C(11)H, C(5)H, C(10)H, C(12)H and C(13)H] in zinc(II), and cadmium(II) complexes did not show any considerable shift. The signal due to free NH₂ [N(1)H] was not observed in zinc(II) as well as cadmium(II) complexes.

The UV–VIS spectrum of the ligand shows only one broad band at 27777 cm⁻¹, which is assigned to $n \rightarrow \pi^*$ of the C=N chromophore. On complexation this band has shifted to lower energy, suggesting the coordination of azomethine nitrogen. The spectrum of the copper(II) complex exhibited only one broad d–d transition

Table 6

IR spectral bands (cm⁻¹) and their assignments in aheb and its metal complexes.

Compound	ν(NH)	v(OH) phenolic	Amide bands			v(C=N)	v(C–O) Phenolic
			I	II	II		
Aheb	3213(m)	2925(b)	1625(s)	1547(s)	1257(m)	1610(s)	1292
[Cu(aheb) ₂]·3H ₂ O	3213(m)	_	1613(s)	1518(m)	1298(m)	1585(s)	1332
[Ni(aheb)2]Cl2·4H2O	3215(m)	-	1605(s)	1541(m)	1276(m)	1592(s)	1336
[Co(aheb) ₂]·3H ₂ O	3214(m)	_	1611(s)	1508(m)	1290(m)	1594(s)	1322
[Mn(aheb) ₂]·3H ₂ O	3215(m)	-	1613(s)	1536(m)	1295(m)	1597(s)	1314
[Zn(aheb) ₂]·3H ₂ O	3212(m)	-	1612(s)	1511(m)	1275(m)	1593(s)	1300
[Cd(aheb) ₂] 3H ₂ O	3213(m)	-	1615(s)	1540(m)	1305(m)	1595(s)	1315

fable 7	
H NMR spectral data of aheb and its zinc(II) and cadmium(II) complexe	es.

Protons	rotons Aheb		Cadmium(II) complex
Chemical Shifts in δ (ppm)			
O(2)H	13.43 (s, 1H)	-	-
N(2)H	10.92 (s, 1H)	10.92 (s, 1H)	10.92 (s, 1H)
C(2)H	6.80 (d, 1H, J = 8.1 Hz)	6.79 (d, 1H, <i>J</i> = 8.2)	6.79 (d, 1H, J = 8.1)
C(5)H and C(10)H	7.64 (m, 2H)	7.63 (m, 2H)	7.63 (m, 2H)
C(11)H	6.61 (t, 1H, <i>J</i> = 7.4 Hz)	6.61 (t, 1H, J = 7.4 Hz)	6.61 (t, 1H, J = 7.4 Hz)
C(12)H and C(13)H	6.91 (m, 2H)	6.91 (m, 2H)	6.91 (m, 2H)
C(15)H	2.47 (s, 3H)	2.47 (s, 3H)	2.47 (s, 3H)

at 14285 cm⁻¹ assigned to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition, which is in conformity with octahedral configuration around the copper ion [23,24]. The two d–d bands in the spectrum of cobalt(II) complex at 14492 and 18867 cm⁻¹ are attributed to ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$ (v₂) and ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}T_{1g}$ (P) (v₃) transitions. These assignments are in good agreement with literature values for octahedral geometry of cobalt(II) complex [24]. No absorptions were observed for the manganese(II) complex indicating it to be a high-spin octahedral complex [25]. The nickel(IV), zinc(II) and cadmium(II) complexes did not show any d–d transitions.

EPR spectrum of copper(II) complex recorded at room temperature and also at liquid nitrogen temperature. The g_{11} and g_{\perp} values are 2.24 and 2.04 respectively. The g_{ave} was calculated to be 2.10. The greater value of g_{11} as compared to g_{\perp} indicated the presence of unpaired electron in $d_{x^2-y^2}$ orbital [26,27].

Mass spectrum of the ligand shows the molecular ion peak at m/z = 269, which correspond to the molecular mass of the ligand. The FAB-mass spectrum of the [Mn(aheb)₂]·3H₂O complex was recorded which show a molecular ion peak (M⁺) at m/z = 654, is indicative of monomeric nature of the complex.

3.4. Magnetic studies

The room temperature effective magnetic moments of 1.79, 4.85, 5.75 BM for copper(II), cobalt(II) and manganese(II) complexes suggest an octahedral geometry around the metal ion centre [28]. Nickel(IV), zinc(II) and cadmium(II) complexes are diamagnetic in nature.

3.5. Thermal studies

The copper(II) and cobalt(II) complexes decompose in two stages. The first step 25-100 °C results in a mass loss of 8.20% (Calcd. 8.25%) and 8.32% (Calcd. 8.31%) respectively, corresponding to the loss of three lattice held water molecules. The temperature range rules out the possibility of coordinated water molecules. In the second step the mass loss of 82.43% (Calcd. 82.33%) and 83.02% (Calcd. 82.92%) in the temperature range 100-456 °C and 100-524 °C corresponds to the loss of ligand molecule in copper(II) and cobalt(II) complexes. A plateau was obtained after heating above 500 °C, which corresponds to the formation of stable CuO and CoO. The weights of CuO and CoO correspond to 9.21% and 8.66% respectively and tallies with the metal analysis.

4. Conclusions

Based on elemental analysis, the complexes synthesised can be formulated as [M(aheb)₂]·3H₂O for copper(II), cobalt(II), manganese(II), zinc(II) and cadmium(II) complexes where as [M(aheb)₂]-·Cl₂·4H₂O for nickel(IV) complex. Aheb act as a tridentate ligand, coordinating through carbonyl oxygen, azomethine nitrogen and phenolic oxygen via deprotonation. The involvement of NH2 group in intramolecular hydrogen bonding with carbonyl oxygen shifts it upfield and has merged with the aromatic proton resonances. It was further supported by the single crystal structure of the ligand and its Ni(IV) complex as well. A lengthening of C=O bond, of Aheb on coordination suggest a decrease in bond order in case of C=O. The bond shortening in case of C=N, may be attributed to electron delocalizations in the coordinated ligand. Magnetic and electronic spectral data suggest distorted octahedral geometries around the metal centres and was further confirmed by single crystal X-ray diffraction studies in case of Ni(IV) complex. FAB mass spectral analysis reveals the monomeric nature of Mn(II) complex. Thermal studies suggest the presence of lattice held water in the complexes reported.

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Appendix A. Supplementary material

The ¹HNMR spectrum of ligand, electronic spectra of cobalt(II) and copper(II) complex, EPR spectrum of copper(II) complex and FAB mass spectra of manganese(II) complex are given in supplementary material. Crystallographic data, bond lengths and bond angles of structure have been deposited with the Cambridge crystallographic Data center, with the deposition number: CCDC 288644. Copies of this information are available free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB₂ 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.molstruc.2014.03.001.

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