

Protonation constant of salicylidene (N-benzoyl)glycyl hydrazone and its coordination behaviour towards some bivalent metal ions

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MS received 23 December 2005; revised 4 April 2006

Abstract. Protonation constant of an unsymmetrical Schiff base, salicylidene(N-benzoyl)glycyl hydrazone (SalBzGH), and formation constants of its complexes have been determined potentiometrically at different temperatures in aqueous dioxane medium. Complexes of SalBzGH with VO(IV), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been prepared. Elemental analyses, pH-metric, molar conductance, magnetic susceptibility, electronic, IR, ESR, XRD (powder) and NMR studies have been carried out to study the coordination behaviour of SalBzGH toward these metal ions. pH-metric and ¹H NMR studies show the presence of two dissociable protons in the ligand. IR and NMR spectra suggest the tridentate nature of the ligand, coordinating as a uninegative species in the Mn(II) complex and as a dinegative species in all the other complexes. Presence of two different conformers of the ligand at room temperature and stabilization of a single conformer upon complex formation have been established from ¹H NMR spectra of the metal-free ligand, Zn(II) and Hg(II) complexes recorded at 296 K. Electronic and ESR spectra indicate highly distorted tetragonal geometry for VO(IV) and Cu(II) complexes. XRD powder patterns of the Zn(II) complexes are indexed for an orthorhombic crystal system.

Keywords. Salicylidene(N-benzoyl)glycyl hydrazone; protonation constant; NMR; coordination behaviour.

1. Introduction

Development of the field of bioinorganic chemistry has increased interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species.¹ Another interesting feature of these molecules is the possibility of coordinating either in the neutral (keto) or in the anionic (imidol) form via the loss of the 'amide' hydrogen. The chelating behaviour of Schiff bases formed by the condensation of acid hydrazides with heteroaromatic aldehydes and ketones have been studied² in our laboratory in order to observe the influence that coordination exerts on their conformation and/or configuration, in connection with the nature of the metal and of the counterion.

We have reported³ that the polydentate ligand, salicylidene(N-benzoyl)glycyl hydrazone (SalBzGH, figure 1), exists in two isomeric forms in the free state at room temperature. However, it assumes only

one configuration when coordinated to the lanthanide(III) ion and prefers to form complexes only in the anionic form. In order to gain more information on the nature of the ligand and its coordination behaviour, we have synthesized complexes of SalBzGH with transition metal ions and carried out potentiometric and spectroscopic studies of the complexes. We report here the results of the above studies.

2. Experimental

All the chemicals used in the present study were of AnalaR grade. N-benzoyl glycine obtained from E

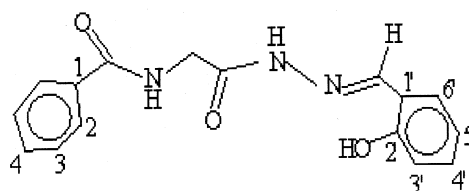


Figure 1. Structure of SalBzGH.

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Merck was used as such for the preparation of its hydrazine derivative. SalBzGH was prepared from the hydrazine derivative as described³ and confirmed from its elemental and spectral data (lit. m.pt. 249°C, N₂H₄ % 11.81; found m.pt. 247°C, N₂H₄ % 11.80, M⁺ at *m/e* 295). Molar conductance was determined in 10⁻³ M DMSO solution at room temperature using a WTW conductivity meter. A digital pH-meter of Systronics-355 with a glass electrode (pH ranges from 0–14) was employed for the potentiometric measurements and a thermostat model (D8-G of Haake Mess-Technick) within an accuracy of ± 0.02°C was used to maintain the temperature. Room temperature magnetic studies were carried out on a Cahn–Faraday electrobalance while the UV-Vis spectra were recorded on a Cary-14 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer in nujol in 4000–200 cm⁻¹ region while ESR spectra were obtained at 77 K in DMSO on a Varian E-line X band ESR spectrophotometer using TCNE as a *g* marker. The XRD (powder) patterns were taken by Phillips X-ray diffractometer PW 1710 using CuK α radiation. ¹H and ¹³C NMR spectra were recorded in DMSO-*d*₆ on a Joel FX- 90Q multinuclear NMR spectrometer at 90 and 22.43 MHz respectively. The mass spectrum of [VO(SalBzGH-2H)(H₂O)] was obtained on a Varian Mat CH-7 Mass spectrometer.

2.1 Preparation and analysis of complexes

[Salicylidene(N-benzoyl)glycyl hydrazonato) aqua metal(II)], [M(SalBzGH-2H)(H₂O)_{*n*}] [M = Co, Ni, *n* = 3; M = VO, Cu, Zn, Hg, *n* = 1], [bis(salicylidene (N-benzoyl) glycyl hydrazonato) manganese(II)], [Mn(SalBzGH-H₂)] and potassium [bis(salicylidene (N-benzoyl) glycyl hydrazonato) cadmate(II)], K₂[Cd(SalBzGH-2H)₂] were prepared by mixing together aqueous solutions of the metal chloride (2.0 mmol in 10 ml), SalBzGH (2.0 mmol in 20 ml) and KOH (4.0 mmol in 20 ml) and adjusting the pH of the resulting solution at ~7 by the controlled addition of 1N acetic acid. The precipitated complexes were digested on a water bath for 0.5 h, cooled, filtered, washed successively with water and ethanol and dried at room temperature.

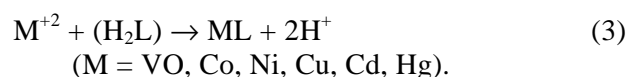
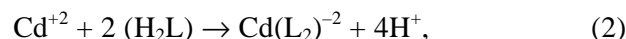
The metal contents were analysed using standard literature procedures.⁴ Nitrogen was microanalysed. Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis.

2.2 Preparation of the reaction mixtures for potentiometric measurements

All the solutions used in the determination of the stability constants of the complexes were prepared in deionized water. The ligand solutions were made in 30% aqueous dioxane media. The metal–ligand ratio was kept constant at 1 : 5 and 1M KNO₃ was used to maintain the ionic strength at 0.05 M. The titrations were carried out over the pH range 2.5–11.5 with standard KOH solution. All the titration solutions were thermostatted at the desired temperatures.

3. Results and discussion

The analytical and physical data along with the molar conductance values of the complexes are summarized in table 1. The table indicates that SalBzGH forms only neutral/deprotonated complexes. It can also be observed that the ligand reacts with the metal chlorides independently of mole ratio. SalBzGH acts as a uninegative species only in case of the Mn(II) complex, while in all the other complexes its behaviour is dinegative. The reactions of the ligand with the metal ions may be given as follows:



All the complexes are stable under ordinary conditions. They are only sparingly/freely soluble in strong coordinating solvents like DMSO and DMF. The weight loss shown by the complexes on heating in the 120–160°C temperature range corresponds to the presence of one water molecule in VO(IV), Cu(II), Zn(II) and Hg(II) complexes and three water molecules in Co(II) and Ni(II) complexes. Their molar conductance values in 10⁻³ M DMSO solutions suggest non-ionic behaviour.⁵

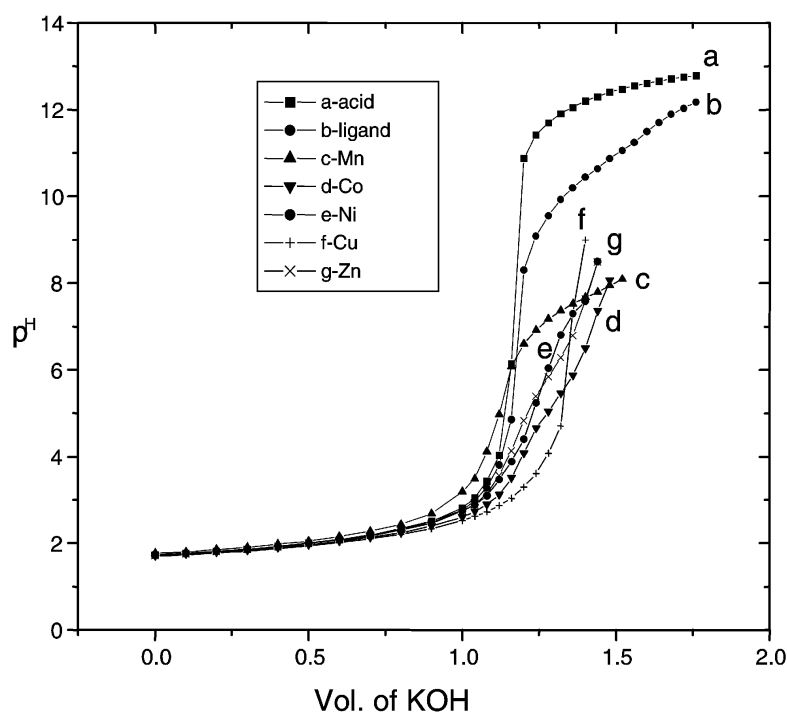
3.1 Protonation and stability constants of the ligand and the complexes

The titration curve of SalBzGH (figure 2) shows two inflection points between pH 4.40 and 12.50 consistent with the liberation of two protons during com-

Table 1. Physical characteristics, analytical data and molar conductances* of the complexes of SalBzGH.

Complex	Colour	Yield (%)	m.p. (°C)	Found (calcd.) %			Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
				M	N ₂ H ₄	N	
Mn(SalBzGH-H) ₂	Dirty yellow	70	182 ^d	7.91 (8.54)	10.06 (9.96)	12.80 (13.05)	29.99
VO(SalBzGH-2H)(H ₂ O)	Green	65	170 ^d	13.21 (13.43)	8.45 (8.44)	10.46 (11.07)	10.61
Co(SalBzGH-2H)(H ₂ O) ₃	Pink	70	>250	14.82 (14.47)	8.00 (7.86)	10.00 (10.31)	5.60
Ni(SalBzGH-2H)(H ₂ O) ₃	Brownish green	70	>250	14.25 (14.42)	7.47 (7.86)	10.35 (10.32)	2.22
Cu(SalBzGH-2H)(H ₂ O)	Green	75	250	16.01 (16.88)	–	10.48 (11.15)	5.71
Zn(SalBzGH-2H)(H ₂ O)	Cream	75	>250	16.88 (17.31)	8.44 (8.47)	10.44 (11.12)	5.32
Hg(SalBzGH-2H)(H ₂ O)	Dirty yellow	65	207	38.80 (39.11)	6.14 (6.24)	8.69 (8.19)	5.14
K ₂ Cd(SalBzGH-2H) ₂	Yellow	60	>250	14.32 (14.39)	8.10 (8.19)	10.29 (10.76)	–

d – decomposition temperature; *in DMSO

**Figure 2.** Titration curves of SalBzGH and its complexes at 30°C at 0.05 M ionic strength.

plexation at these pH ranges. The protonation constant of SalBzGH and formation constants of its complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions are obtained at 10, 20, 30, 40 and 50°C using Bjerrum's half \bar{n} -value method⁶ as modi-

fied by Irving and Rossetti;⁷ the values are shown in table 2. The first and second protonation constants, $\log K_n H$ ($n = 1, 2$) are evaluated from the proton-ligand formation curves (figure 3) corresponding to 0.5 and 1.5 on the \bar{n}_H scale. The first protonation

Table 2. Protonation constants of SalBzGH, formation constants ($\log K_n$) and other thermodynamic parameters for its complexes at different temperatures (T) at constant ionic strength (0.05 M) in 30% aqueous dioxane media.

T (°C)	Stability constant	H(I) ^a	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
10	Log K_1	15.60	11.25	13.90	13.00	15.25	12.40
	Log K_2	11.20	10.30	—	—	—	—
	$-\Delta G^\circ$	—	27.52	18.00	16.84	19.75	16.06
20	Log K_1	15.60	10.90	13.25	12.65	14.85	12.10
	Log K_2	10.80	10.05	—	—	—	—
	$-\Delta G^\circ$	—	28.09	17.77	16.96	19.91	16.22
30	Log K_1	14.90	10.60	12.55	12.00	14.50	11.90
	Log K_2	10.60	10.00	—	—	—	—
	$-\Delta G^\circ$	—	28.56	17.40	16.64	20.10	16.50
	$-\Delta H^\circ$	—	57.97	38.13	41.33	36.61	33.97
	$-\Delta S^\circ$	—	97.04	68.42	81.50	54.47	57.66
40	Log K_1	13.35	9.10	11.60	10.90	13.05	10.35
	Log K_2	10.15	8.45	—	—	—	—
	$-\Delta G^\circ$	—	25.14	16.61	15.61	18.69	14.82
50	Log K_1	13.05	8.50	10.85	10.05	12.75	9.75
	Log K_2	10.05	7.90	—	—	—	—
	$-\Delta G^\circ$	—	24.24	16.04	24.24	18.85	14.41

ΔG° = change in free energy (kcal/mol); ΔH° = change in enthalpy (kcal/mol); ΔS° = change in entropy (cal/deg/mol)

^aH(1) values are $\log K_1H$ and $\log K_2H$ at 0.05 M ionic strength

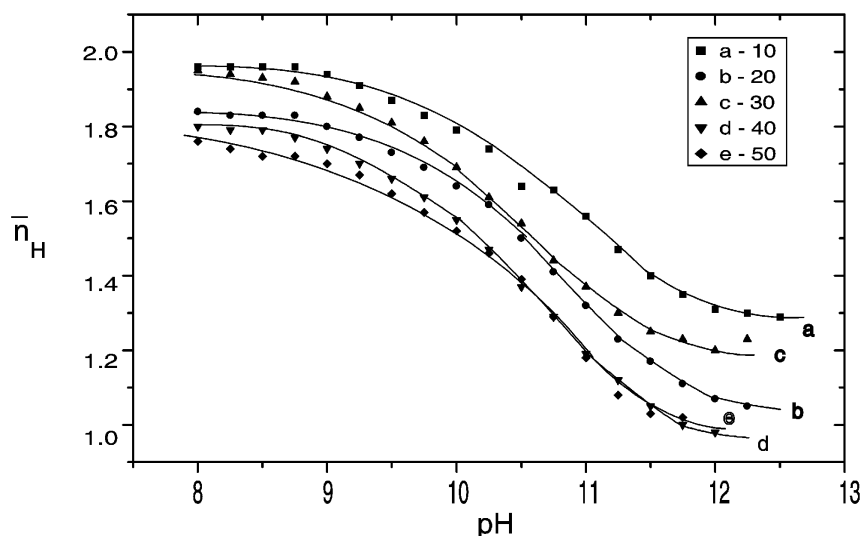


Figure 3. Proton ligand formation curves of SalBzGH at different temperatures and 0.05 M ionic strength.

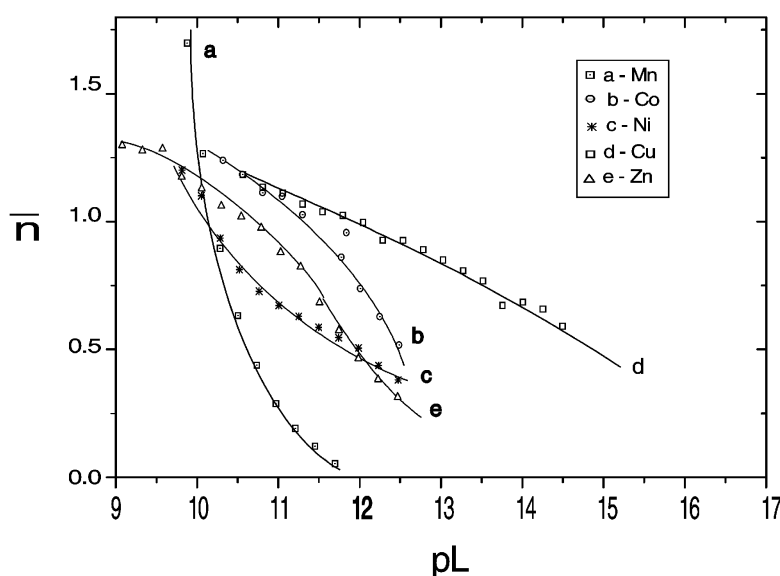
constant, $\log K_1H$ can not be evaluated from the protonation curves as the curves fall between 0.99 and 2.00 on the \bar{n}_H scale. Therefore, the values of $\log K_1H$ are calculated using the relationship given below:⁸

$$\log K_1H = 2\text{pH} (\bar{n}_H = 1.0) - \text{pH} (\bar{n}_H = 1.5).$$

The maximum value of \bar{n} in the metal–ligand formation curve (figure 4) of Mn(II) complex is 1.8 indicating formation of both 1 : 1 and 1 : 2 complexes. However, formation of only 1 : 1 type of complex is suggested for the Co(II), Ni(II), Cu(II) and Zn(II) complexes as the values of \bar{n} in their formation curves do not exceed 1.2 on the \bar{n} scale. The calcu-

Table 3. m_{eff} values, electronic spectral bands and assigned transitions of the complexes^a.

Complexes	m_{eff} (BM)	Band maxima (cm ⁻¹)	Transitions
[VO(SalBzGH-2H)(H ₂ O)]	1.77	12048 17241 23256	${}^2b_{2g} \rightarrow {}^2e_g^*$ $\rightarrow {}^2b_{1g}^*$ $\rightarrow {}^2a_{1g}^*$
[Mn(SalBzGH-H) ₂]	5.98	—	—
[Co(SalBzGH-2H)(H ₂ O) ₃]	4.57	9524 12500 19048	${}^4T_{1g} \rightarrow {}^4T_{2g} (F)$ $\rightarrow {}^4A_{2g} (F)$ $\rightarrow {}^4T_{1g} (P)$
[Ni(SalBzGH-2H)(H ₂ O) ₃]	3.19	10226 15152 25000	${}^3A_{2g} \rightarrow {}^3T_{2g} (F)$ $\rightarrow {}^3T_{1g} (F)$ $\rightarrow {}^3T_{1g} (P)$
[Cu(SalBzGH-2H)(H ₂ O)]	1.82	16667	${}^2B_{1g} \rightarrow {}^2B_{2g} (D)$

^aThe spectra are recorded in nujol mull**Figure 4.** Formation curves of the complexes at 30°C (0.05 M).

lated overall changes in free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) for the complexation reactions are also included in table 2. The values indicate the spontaneity and exothermic nature of all the complexation reactions. ΔS° is negative for all the complexes, which can be attributed to the extensive solvation of the metal chelates in aqueous-organic media.

3.2 Magnetic susceptibility measurements and electronic absorption spectra

The m_{eff} values and the electronic absorption band of the complexes along their respective assignments

are given in table 3. The magnetic moments of VO(IV), Mn(II) and Cu(II) complexes are normal giving no indication of their stoichiometry. However, the electronic spectrum of VO(IV) complex shows absorptions at 12048, 17241 and 23256 cm⁻¹ assignable to ${}^2b_{2g} \rightarrow {}^2e_g^*$, ${}^2b_{1g}^*$, and ${}^2a_{1g}^*$ transitions, respectively, assuming square pyramidal geometry⁹ around the metal ion. A square planar geometry¹⁰ of the Cu(II) complex can be invoked from its electronic spectral band at 16667 cm⁻¹ assignable to ${}^2B_{1g} \rightarrow {}^2B_{2g} (D)$ transition. The m_{eff} value of Co(II) complex (4.57 BM) is slightly lower than the expected value for octahedral geometry; however the electronic spectrum of the complex yields three bands at

9524, 12500 and 19048 cm^{-1} assignable to ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F)$ and ${}^4T_{1g}(P)$ transitions respectively, suggesting the metal ion is in octahedral stoichiometry.¹¹ The spectral bands and the m_{eff} values of the Ni(II) complex are characteristic of an octahedral coordination around the metal ion.¹¹

3.3 Infrared spectra

The bonding sites of SalBzGH involved in complexation with the metal ions have been assigned by a careful comparison of the IR spectra of the complexes with that of the parent ligand as given in table 4 (see supplementary material). The two strong bands at 1700 and 1630 cm^{-1} in the spectrum of SalBzGH are due to the amide I frequencies of the $>\text{C}=\text{O}$ groups of the hydrazide and the benzamide moieties respectively, and the medium intensity bands at 1565 and 1530 cm^{-1} may be assigned to the corresponding amide II frequencies. In the spectra of the complexes, the amide bands of the benzamide carbonyl group appear unaffected suggesting non-coordination of the above group. However, such amide bands of the hydrazide $>\text{C}=\text{O}$ group disappear and a sharp band diagnostic of $>\text{C}=\text{N}-\text{N}=\text{C}<$ group appears at 1620–1600 cm^{-1} in the spectra of the complexes except in that of the Mn(II) complex. The appearance of this new band in the spectra of the complexes suggests formation of neutral complexes in which the ligand coordinates in its enol form. It can best be explained by assuming the destruction of the hydrazide carbonyl group through amide \leftrightarrow imidol tautomerism and subsequent coordination of the imidol oxygen.¹² This is further supported by the appearance of new peaks characteristic of $n(\text{NCO}^-)$ in the 1570–1545 and 1345–1300 cm^{-1} regions in the spectra of the complexes.¹² In the spectrum of the Mn(II) complex, these amide bands show negative shift to 1680 and 1535 cm^{-1} showing the coordination of the carbonyl oxygen to Mn(II) ion in the amide form.¹³ Coordination through the azomethine nitrogen¹⁴ is suggested on the basis of the observed negative shift (10–30 cm^{-1}) in the $n(\text{CN})$ band and a positive shift (10–40 cm^{-1}) in the $n(\text{NN})$ band in the spectra of all the complexes. The observed hypsochromic shift (15–25 cm^{-1}) of the $n_{\text{sym}}(\text{CO})_{\text{phenolic}}$ band and simultaneous disappearance of the $n(\text{OH})_{\text{phenol}}$ from the spectra of all the complexes indicate participation of the phenolate oxygen in bonding.¹⁵ A strong band at 970 cm^{-1} in the spectrum of VO(IV) complex is tentatively assigned to ($\nu = 0$)

stretching mode.¹⁵ The medium intensity bands at 425–380 cm^{-1} are assigned to the $n(\text{MO})$ mode.

3.4 ESR spectra

The ESR spectrum of the Mn(II) complex at LNT shows a line shape which is indicative of unsymmetrical six-coordination of the Mn(II) ion. The spectrum of VO(IV) complex at RT shows normal eight line isotropic features revealing hyperfine splitting of the ${}^{51}\text{V}$ nucleus while its frozen solution spectrum is anisotropic showing parallel and perpendicular features separately. The absence of the superhyperfine splitting in the spectrum at RT and the trend of g -values calculated from the frozen spectrum ($g_{\parallel} < g_{\perp} < 2$) show that the unpaired electron is in the $b_{2g}(d_{xy})$ orbital localized on the metal^{16,17}. The frozen solution spectrum of the Cu(II) complex is characteristic of axial symmetry and the trend $g_{\parallel} > g_{\perp} > 2.0023$ indicates tetragonal elongation along the z -axis and presence of an unpaired electron in the $b_{1g}(d_{x^2-y^2})$ orbital.¹⁷ The g value (2.276) suggests the Cu^{+2} to be in a more covalent environment¹⁸ which is further supported by small $\langle A \rangle$ value of 67.8 G. The bonding parameter (a^2) is found to be 0.76, which shows an appreciable covalency in the in-plane s -bonding.^{19,20}

3.5 X-ray diffraction studies

All the 23 lines obtained for the Zn(II) complex are successfully indexed.²¹ The indexing of the patterns yields the lattice constants, $a = 23.5748 \text{ \AA}$, $b = 9.0683 \text{ \AA}$ and $c = 8.0162 \text{ \AA}$ indicating an orthorhombic system for $[\text{Zn}(\text{SalBzGH-2H})(\text{H}_2\text{O})]$.

3.6 ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra

Selected ${}^1\text{H}$ NMR spectral bands of SalBzGH and its Zn(II) and Hg(II) complexes along with their assignments are given in table 5 (see supplementary material). SalBzGH is reported³ to show a dynamic equilibrium between two isomers over the 298–368 K range. However, a single isomer gets stabilized upon complex formation. This is indicated by coalescence of the two triplets of $\text{C}_6\text{H}_5\text{CONHCH}_2-$ (d , 8.66^t and 8.88^t) observed in the ${}^1\text{H}$ NMR spectrum of the ligand characterizing the two conformers of SalBzGH into a single triplet in the spectra of Zn(II) (d , 8.93^t) and Hg(II) (d , 8.98^t) complexes respecti-

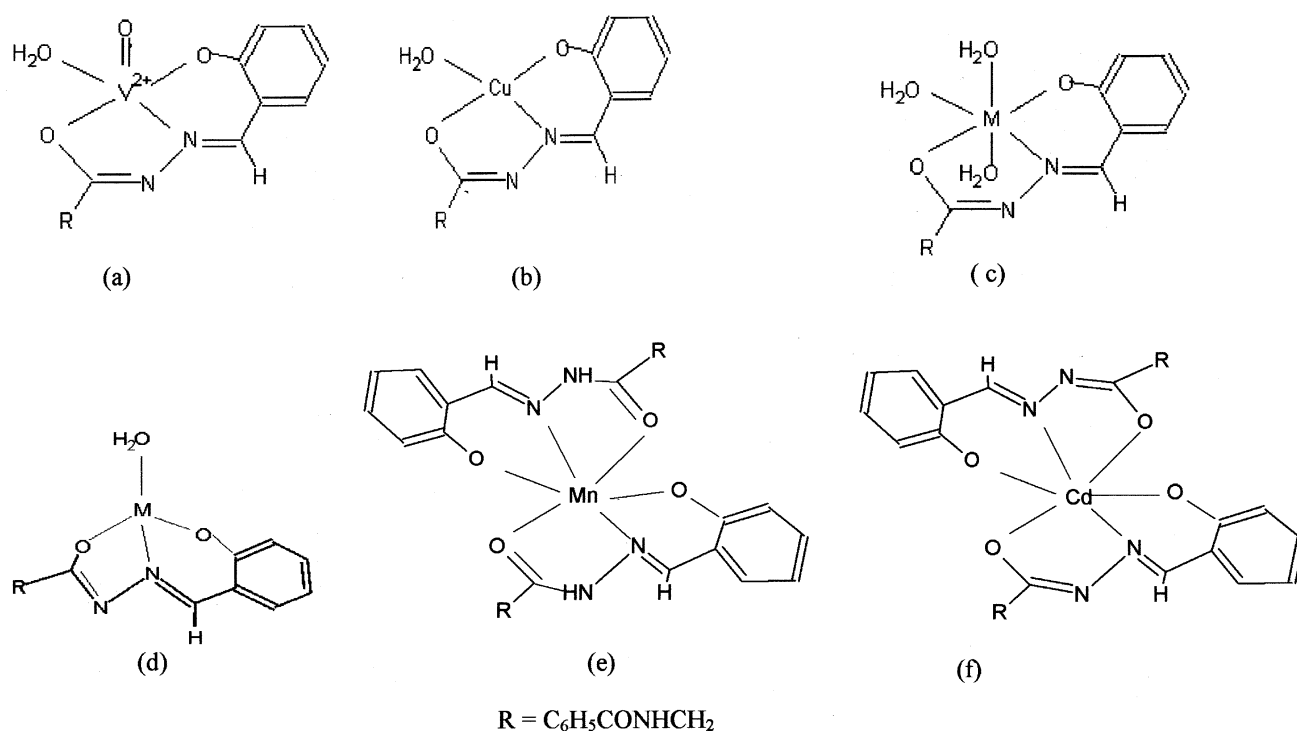


Figure 5. Proposed structures of the complexes (a) VO(IV), (b) Cu(II), (c) M = Co(II), Ni(II), (d) M = Zn(II), Hg(II), (e) Mn(II) and (f) Cd(II).

vely. The signals due to $-\text{C}_6\text{H}_4\text{OH}$ and $\text{RNHC}=\text{O}$ disappear in the spectra of the complexes. The above observations support deprotonation of the phenolic $-\text{OH}$ and the hydrazidic $-\text{NH}$ and consequent coordination of SalBzGH as a dinegative species. The downfield shift (δ , 0.22 and 0.15) of the $-\text{N}=\text{CH}-$ signals observed in the spectra of the above complexes suggest interaction of the azomethine nitrogen²² in the complexes. Further, there is a high-field shift of the resonance signals due to the salicyloyl ring protons in the spectra of the complexes. Such a shift may be due to an increase in electron density through electron delocalization in the di-deprotonated form of the ligand. This indirectly supports coordination of SalBzGH in its deprotonated form.

The numbering scheme of the carbon atoms in the ¹³C NMR spectrum of SalBzGH is as shown in figure 1. The room temperature ¹³C NMR spectrum of the ligand (table 6 in supplementary material) is compatible with two different conformers while the spectrum at 368 K corresponds to a single conformer. The shifts in the $-\text{C}(\text{O})\text{NHN}=\text{C}<$ and $-\text{C}(\text{O})\text{NHN}=\text{C}>$ signals in the spectra of the Zn(II) and Hg(II) complexes suggest coordination through the hydrazidic carbonyl oxygen²³ and azomethine nitrogen.²⁴ The

upfield shifts of the salicyloyl ring carbon atoms are compatible with electron delocalization which in turn supports coordination of SalBzGH as a dinegative species through phenolate oxygen.²⁵ However, the resonance signals due to $\text{C}_6\text{H}_5\text{C}(\text{O})\text{NH}-$ and the phenyl ring carbons suffer no significant shift in the spectra of the complexes indicating non-participation of the benzamide carbonyl group in coordination.

3.7 Mass spectral studies

The mass spectrum of $[\text{VO}(\text{SalBzGH}-2\text{H})(\text{H}_2\text{O})]$ obtained with an energy of about +1.5 a.m.u. at 220°C includes some very weak peaks corresponding to $m/e >$ molecular mass number, which is most likely to suggest the rearrangement of the fragments or collision of the molecular ions with neutral atoms or molecules.²⁶ The base peak at (M 134) m/e 242 for the fragment due to the loss of the benzamide moiety, $\text{C}_6\text{H}_5\text{CO}(\text{NH})\text{CH}_2-$, and the next intense peak with 80% intensity at (M 152) m/e 224 of the fragment results from the loss of $\text{C}_6\text{H}_5\text{CO}(\text{NH})\text{CH}_2-$ group and the coordinated water are taken as confirmation of the molecular ion peak (M^+) at m/e 377 which ap-

pears with 10% intensity. These peaks are in agreement with the composition and structure of the complex proposed based on the elemental and spectral data.

4. Conclusion

The analytical data suggest that SalBzGH can form complexes in both 1 : 1 and 1 : 2 ratio and the complexes formed behave as non-electrolytes in DMSO. pH-metric and ^1H NMR studies show the presence of two dissociable protons in the ligand. IR, ^1H and ^{13}C NMR spectra suggest tridentate behaviour of SalBzGH coordinating as a uninegative species through the hydrazidic carbonyl oxygen, azomethine nitrogen and phenolate oxygen in Mn(II) complex and as a dinegative species bonding through enolate oxygen of the hydrazidic carbonyl group, azomethine nitrogen and phenolate oxygen in all the other complexes. Figure 5 shows the proposed tentative structures of the complexes.

Acknowledgements

The authors thank the Authorities of the Banaras Hindu University and the Manipur University for encouragement and acknowledge the University Grants Commission and Council of Scientific and Industrial Research, New Delhi for financial assistance. Recording of ESR spectra by Regional Sophisticated Instrumentation Centre, Indian Inst. Technol. Bombay, Mumbai is also acknowledged.

Supplementary material: Tables 4–6 containing the IR and NMR data can be seen on the web version of this paper.

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