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LIGATIONAL BEHAVIOR OF FURFURYLIDENE(N-BENZOYL)GLYCYL HYDRAZONE TOWARD SOME TRANSITION METAL IONS

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ABSTRACT

Furfurylidene(*N*-benzoyl)glycyl hydrazone, FBzGH, has been synthesized and characterized. Transition metal complexes of the formulae $[M(FBzGH)_2Cl(H_2O)]Cl (M = Mn, Cu, Zn, Cd,$ Hg), $[Co(FBzGH)_2]Cl_2 \cdot H_2O$ and $[Ni(FBzGH)_2Cl_2] \cdot H_2O$ were isolated from acidic solutions and the complexes $[M(FBzG)_2$ $(H_2O)_2] (M = Co, Ni, Cu)$, from neutral solutions. Elemental analyses, molar conductances, magnetic susceptibilities, electronic, pHmetric, ESR, IR, and NMR studies have been carried out on these complexes to illuminate the ligational behavior of FBzGH toward the divalent metal ions. Formation constants of the metal chelates were determined pH-metrically in aqueous dioxane. IR and NMR

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spectra suggest a bidentate nature of the hydrazone coordinating as a neutral species in the adducts and as a uninegative one in the neutral complexes. ¹H NMR spectra indicate the presence of two different conformers of the ligand at room temperature even after complexation. However, these spectra show coalescence of the peaks at a temperature higher than 340 K indicating that one of the conformers gets stabilized at a higher temperature. A highly shielded chemical shift value of (113). Cd NMR suggests a strongly bound but weakly coordinated Cd²⁺ ion.

INTRODUCTION

The chemistry of hydrazones has been intensely investigated owing to their coordinative capability (1), their pharmacological activity (2), and their use in analytical chemistry as metal extracting agents (3). We, therefore, have undertaken a systematic investigation of the coordination behavior of a number of hydrazones derived from interactions of amino acid hydrazides with different aldehydes and ketones, with 3d (4,5) and 4f (6,7) block elements. We report here the results of our studies on the ligational behavior of a hydrazone derivative obtained from the condensation of *N*-benzoyl glycine hydrazide with furfuraldehyde, furfurylidene(*N*-benzoyl)glycyl hydrazone (Fig. 1) and characterization of the complexes of the hydrazone with some bivalent transition metal ions.

RESULTS AND DISCUSSION

Characterization of FBzGH

The solid state IR spectrum of FBzGH shows bands at 1675, 1545 cm⁻¹ and 1630, 1520 cm⁻¹, which may be assigned to the amide I and II frequencies of the hydrazide and benzamide carbonyl groups while the bands observed at 1570 and 1015 cm⁻¹ are due to γ (C=N) and γ (N–N) modes, respectively.



Figure 1. Structure of FBzGH.

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In the ¹H NMR spectrum, the hydrazide $-N\underline{H}$ and the $-NC\underline{H}$ groups exhibit sharp singlets at δ 11.70 and 8.30 whereas the furane and phenyl ring protons are observed as multiplets at δ 8.07–7.67 and 7.00–6.73, respectively. The doubling of the signals due to the benzamide $-N\underline{H}$ and the $-C\underline{H}_2$ protons at δ 9.07, 8.67 and 4.53, 4.13 shows the existence of two predominant isomers at room temperature (296 K). As the temperature is raised, coalescence of the isomeric peaks is clearly observed over the range of temperature 296–348 K, as shown in Figure 2. This observation is consistent with a single isomer predominating, or two or more isomers being in the fast exchange limit of the NMR time scale. The spectrum after deuterium exchange is devoid of the signals due to the benzamide $-N\underline{H}$ and hydrazide $-N\underline{H}$ groups.

All the signals in the ¹³C NMR spectrum have been approximated applying the substituent additivity (8). The numbering of the carbon atoms is as shown in Figure 1. The ¹³C-NMR spectrum of the ligand corresponds to the presence of more than one isomer of the ligand at 296 K and the predominance of only



Figure 2. ¹H-NMR spectral peaks of (I) FBzGH and (II) $[Cd(FBzGH)_2Cl(H_2O)]Cl$ as a function of temperature. (a) Benzamidic $-NH^-$ and (b) $-CH_2^-$ signals.



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Figure 3. Mass spectrum of FBzGH.

one isomer at 348 K. The hydrazide $\geq \underline{C}O$ absorbs at 169.25 ppm whereas the benzamide $\geq \underline{C}O$ shows two sharp peaks at 166.87 and 166.12 ppm.

In the mass spectrum (Fig. 3), the base peak observed at 105 m/e corresponds to C₆H₅CO⁺. The molecular ion peak (M⁺) appears with 40% intensity at m/e = 271. The possible fragments of FBzGH corresponding to the other peaks with appreciable intensity are shown in Figure 4.

Characterization of the Complexes

Analytical data of the complexes (Table 1) indicates that FBzGH forms two types of complexes as a function of pH i.e., addition/chloro and neutral/ deprotonated complexes having 1:2 (metal:ligand) ratio as represented by the following equations:

$$MCl_2 \cdot mH_2O + 2FBzGH H \stackrel{\text{EtOH}}{\longrightarrow} H M(FBzGH)_2Cl_2H_2O + (m-1)H_2O$$
$$MCl_2 \cdot mH_2O + 2FBzGH H \stackrel{\text{NaOH}}{\longrightarrow} H [M(FBzG)_2(H_2O)_2] + (m-2)H_2O$$
$$+ 2HCl$$

All of the complexes are stable under ordinary conditions and decompose at specific temperatures. They are insoluble in water and common organic solvents except DMF and DMSO. Their molar conductances (9) in 0.001 *M* DMSO solutions show the divalent Mn, Cu, Zn, Cd, Hg adducts to be 1:1 electrolytes, Copyright @ Marcel Dekker, Inc. All rights reserved.



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Figure 4. Possible fragments of FBzGH.

the Co adduct to be a 1:2 electrolyte and the remaining complexes nonionic species.

Magnetic Moments and Electronic Spectral Data

The μ_{eff} values and the band maxima observed in the electronic spectra of the complexes are given in Table 2. The μ_{eff} values of Mn(II) and of both the Cu(II) complexes are as expected for five and one unpaired electrons and do not infer any information regarding their stereochemistries. However, the electronic spectra of the Cu(II) complexes show bands at 14,286 and 15,385 cm⁻¹ in the adduct and neutral complexes, respectively, due to the transition ${}^{2}\text{Eg} \rightarrow 2T_{2g}(D)$ indicating a

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Table 1. Colour, Analytical, and Molar Conductance Data of the Complexes of FBzGH

Complex Empirical Formula:		Yield	mn		Found (Calcd) %		Molar Conductance $(\Omega^{-1} \text{ cm}^2)$
(Formula Weight)	Colour	(%)	(°C)	Metal	Cl	Ν	N_2H_4	mol^{-1})
FBzGH	Light	80	192	-	-	15.44	11.80	-
C ₁₄ H ₁₃ N ₃ O ₃ ; (271)	brown					(15.50)	(11.81)	
[Mn(FBzGH) ₂ - Cl(H ₂ O)]Cl	Light	70	112 ^d	8.21	10.30	11.99	9.00	20.93
MnC ₂₈ H ₂₈ N ₆ O ₇ Cl ₂ ; (686)	yellow			(8.01)	(10.35)	(12.25)	(9.33)	
[Cu(FBzGH) ₂ - Cl(H ₂ O)]Cl	Light	65	200 ^d	9.10	10.27	11.89	-	-
$CuC_{28}H_{28}-$ N ₆ O ₇ Cl ₂ ; (695)	green			(9.15)	(10.22)	(12.09)		
[Zn(FBzGH) ₂ - Cl(H ₂ O)]Cl	Light	65	157 ^d	9.50	10.22	11.78	9.59	26.03
$ZnC_{28}H_{28}-$ N ₆ O ₇ Cl ₂ ; (697)	yellow			(9.39)	(10.20)	(12.06)	(9.19)	
[Cd(FBzGH) ₂ - Cl(H ₂ O)]Cl	Cream	75	172 ^d	14.97	9.88	10.97	8.43	21.50
$CdC_{28}H_{28}-$ N ₆ O ₇ Cl ₂ ; (744)				(15.12)	(9.55)	(11.30)	(8.61)	
[Hg(FBzGH) ₂ - Cl(H ₂ O)]Cl	Cream	60	155 ^d	24.27	8.20	10.12	7.68	28.11
$HgC_{28}H_{28}-$ N ₆ O ₇ Cl ₂ ; (832)				(24.12)	(8.54)	(10.10)	(7.70)	
[Co(FBzGH) ₂]- Cl ₂ .H ₂ O	Green	68	182 ^d	8.40	10.01	12.17	9.27	99.16
CoC ₂₈ H ₂₈ N ₆ O ₇ Cl ₂ ; (690)				(8.54)	(10.29)	(12.18)	(9.28)	
[Ni(FBzGH) ₂ Cl ₂]H ₂ O	Light	68	219 ^d	8.23	10.00	12.03	9.50	12.45
$NiC_{28}H_{28}N_6O_7Cl_2$; (690)	green			(8.51)	(10.29)	(12.18)	(9.28)	
$[Co(FBzG)_2(H_2O)_2]$	Pink	70	206 ^d	9.30	_	13.21	10.00	_
CoC ₂₈ H ₂₈ N ₆ O ₈ ; (635)				(9.28)		(13.23)	(10.07)	
[Ni(FBzG) ₂ (H ₂ O) ₂]	Light	70	200 ^d	9.05	-	12.90	10.05	_
NiC ₂₈ H ₂₈ N ₆ O ₈ ; (634)				(9.25)		(13.23)	(10.07)	
$[Cu(FBzG)_2(H_2O)_2]$	Green	70	267 ^d	9.70	-	13.13	_	_
CuC ₂₈ H ₂₈ N ₆ O ₈ ; (640)				(9.94)		(13.13)		

d: Decomposition temperature.

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distorted-octahedral geometry (10) of the complexes. The [Ni(FBzGH)₂Cl₂] · H₂O and [Ni(FBzG)₂(H₂O)₂] complexes show the magnetic moments 3.26 and 3.28 B.M., respectively, which correspond to an octahedral chromophore that is further supported by the electronic bands observed at 9091 (γ_1), 14,085 (γ_2), and 23,810 (γ_3) cm⁻¹ and 10,020 (γ_1), 14,670 (γ_2), and 22,320 (γ_3) cm⁻¹ due to the transitions ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$, ${}^{3}T_{1g}(F)$, and ${}^{3}T_{1g}(P)$, respectively, of an octahedral stereochemistry (11). A tetrahedral (12) geometry has been assigned to



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Table 2. μ_{eff} Values, Electronic Absorption Bands, and Assigned Transitions of the Complexes^{*a*}

Complexes	$\mu_{\rm eff}$ (B.M.)	Bands (cm ⁻¹)	Transitions
[Mn(FBzGH) ₂ Cl(H ₂ O)]Cl	5.27	18868	${}^{6}A_{1\sigma} \rightarrow {}^{4}T_{1\sigma}(G)$
[Cu(FBzGH)2Cl(H2O)]Cl	2.00	12346 sh, 14286	$^{2}B_{1g} \rightarrow ^{2}A_{1g}, ^{2}B_{2g}$
$[Cu(FBzG)_2(H_2O)_2]$	2.08	15385	$^{2}B_{1g} \rightarrow ^{2}B_{2g}$
[Ni(FBzGH)2Cl2]H2O	3.26	9091, 14085	$^{3}A_{2g} \rightarrow ^{3}T_{2g}, ^{3}T_{1g}(F)$
		23810	$\rightarrow {}^{3}T_{1g}(P)$
$[Ni(FBzG)_2(H_2O)_2]$	3.28	10020, 14670	${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}, {}^{3}T_{1g}(F)$
		22320	$\rightarrow {}^{3}T_{1g}(P)$
$[Co(FBzGH)_2]Cl_2 \cdot H_2O$	4.05	6452	${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$
		14493, 15038, 16000	${}^{4}A_2 \rightarrow {}^{4}T_1(P)$
$[Co(FBzG)_2(H_2O)_2]$	4.67	9901, 13793	${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}, {}^{4}T_{2g}(F)$
		19802	$\rightarrow {}^{4}T_{1g}(P)$

sh = Shoulder.

^aThe spectra were recorded as Nujol mulls.

 $[Co(FBzGH)_2]Cl_2 \cdot H_2O$ based on its μ_{eff} value (4.05 B.M.) and electronic absorption bands observed as a broad band at 6450 cm⁻¹ that may be due to the transition, ${}^{4}A_2 \rightarrow {}^{4}T_1(F)$ and a multiplet at 14,493, 15,038, 16,000 cm⁻¹ due to the transition ${}^{4}A_2 \rightarrow {}^{4}T_1(P)$ for a d⁷ tetrahedron. The magnetic moment of $[Co(FBzG)_2(H_2O)_2]$ is 4.67 B.M. and the electronic bands observed at 9901, 13,793, and 19,802 cm⁻¹ assignable to the transitions, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$, ${}^{4}T_{2g}(F)$, and ${}^{4}T_{1g}(P)$, respectively, suggest an octahedral geometry (10) around the metal ion.

Electron Spin Resonance Spectra

The ESR spectra of both Cu(II) complexes are isotropic at room temperature. However, the spectra are anisotropic at LNT and are characteristic of axial symmetry. The g_{\parallel} and g_{\perp} values are 2.295 and 2.041 for the Cu(II) adduct and 2.276 and 2.061 for the Cu(II) deprotonated complex, respectively. The trend $g_{\parallel} > g_{\perp} > g_{\rm e}$ indicates tetragonal elongation along the *z*-axis and the presence of the unpaired electron in the $b_{1g}(d_{x2-y2})$ orbital (13). Large A_{\parallel} values,140 and 163.3 G, and in-plane σ -bonding parameters (α^2) calculated for the Cu(II) complexes (0.71 and 0.76) depict a predominant covalent in-plane bonding (14) in these complexes.

Stability Constants of Co(II), Ni(II), and Cu(II) Complexes

The proton-ligand constants, log K_1H , and the metal-ligand stability constants, log K_1 , for the formation of the cobalt, nickel, and copper complexes with FBzGH were obtained using Bjerrum's half *n*-value method (15) modified by



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Table 3. Protonation Constants of FBzGH, Metal–Ligand Stability Constants, and Other Thermodynamic Parameters for the Co(II), Ni(II), and Cu(II) Complexes of FBzGH at Different Temperatures (T) and Ionic Strengths (μ)

	H(I)	Co(II)	Ni(II)	Cu(II)
Protonation and metal-ligand stability constants ^{<i>a</i>}				
When μ is varied				
0.00 M	-	11.4000	11.6000	12.4000
0.05 M	12.4000	13.5000	12.7050	13.2575
0.10 M	12.2075	13.2500	12.5555	13.2500
0.15 M	11.9500	12.2000	12.5025	13.1500
0.20 M	11.7050	11.9000	13.3025	13.0050
When T is varied				
10°C	12.4500	15.5000	12.9050	13.9050
20°C	11.7050	14.2550	12.9000	13.5550
30°C	11.9025	13.5000	12.7050	13.2575
40°C	12.5050	13.2500	12.3025	13.4000
50°C	12.7050	13.1000	11.9050	13.6550
Other thermodynamic parameters				
$-\Delta G^{\circ}$				
$T = 10^{\circ} \mathrm{C}$		20.0726	16.7121	18.0071
$T = 20^{\circ} \mathrm{C}$		19.1126	17.2959	18.1741
$T = 30^{\circ} \text{C}$		18.7181	17.6158	18.3819
$T = 40^{\circ} \mathrm{C}$		18.9778	17.6207	19.1927
$T = 50^{\circ} \text{C}$		19.3624	17.5962	20.1827
$-\Delta H^{\circ}$ (kcals/mol) at $T = 30^{\circ}C$		2.5932	1.1443	1.3925
ΔS° (cals/deg/mol) $T = 30^{\circ}C$		53.2170	54.3614	56.1000

 ΔG° = Change in free energy; ΔH° = Change in enthalpy; ΔS° = Change in entropy. ^{*a*}H(I) Values under these are Log K₁H at 30°C; Co(II), Ni(II), and Cu(II) values under these are Log K₁ at 30°C.

Irving and Rossotti (16). The calculated (17) free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) data are included in Table 3. The proton–ligand formation curve (Fig. 5) shows that FBzGH loses only one proton whereas the metal-ligand formation curve (Fig. 6) indicates the metal ligand stoichiometry to be 1:2 in these complexes. ΔG° values have been found to be negative suggesting spontaneity of the formation of the complexes. ΔG° values also indicate that low temperature favors formation of the Co(II) complexes and high temperature favors formation of the Ni(II) and Cu(II) complexes.

Infrared Spectra

The IR frequencies of the selected groups of the ligand and its complexes are included in Table 4 along with the assignments. In order to avoid the complications

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Figure 5. Proton ligand formation curves of FBzGH at 10, 20, 30, 40, and 50°C at 0.05 *M* ionic strength.

due to intermolecular H-bonding, comparison of the spectra of the complexes has been made with the solution spectrum of the ligand. The positions of the amide I and II bands of the benzamide moiety remain unchanged in the spectra of all the complexes indicating noncoordination of this group, and the retention of these bands at 1630 and 1550 cm⁻¹ shows the existence of H-bonding even in the complexes. The amide bands of the hydrazidic carbonyl group undergo a bathochromic shift, 40-65 cm⁻¹ and 5-55 cm⁻¹, in the spectra of the adducts suggesting coordination through the above group (18) in these complexes. All of these amide bands of the hydrazide group, however, are absent in the spectra of the deprotonated complexes while a sharp band diagnostic of the >C=N-N=C<group appears at 1600 cm⁻¹ indicating enolization of the hydrazidic carbonyl group through amide \leftrightarrow imidol tautomerism and subsequent coordination of the imidol oxygen (19) to the M^{2+} ion in the deprotonated complexes. The appearance of two new peaks characteristic of γ (NCO⁻) at 1565 and 1305 cm⁻¹ in the spectra of the neutral complexes also supports the coordination of the imidol group (19). Complexation through the azomethine nitrogen (20) has been inferred from the observed bathochromic shift (25–35 cm⁻¹) in γ (C=N) and the hypsochromic shift (5–20 cm⁻¹) in the γ (N–N) bands, in the spectra of the complexes. The furane ring vibrations (21) at 1500, 885, and 750 cm^{-1} in the spectrum of the metal-free FBzGH remain practically unaffected after complexation indicating nonparticipation of the ring oxygen in bonding. The medium intensity bands in the ranges 385–355, 340–320, and 305–250 cm^{-1} tentatively may be attributed to the

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Figure 6. Formation curves of Co(II), Ni(II), and Cu(II) complexes of FBzGH at 30° C (0.05 *M*).

 γ (M–O), γ (M–N), and γ (M–Cl) modes (22), respectively. The doubling feature of the γ (Ni–Cl) band shows that the two chlorine atoms are *cis* to each other.

Nuclear Magnetic Resonance Spectra

The ¹H and ¹³C NMR spectra of the ligand and the Zn(II), Cd(II), and Hg(II) adduct complexes were recorded in DMSO-d₆ solution and the spectral data are included in Tables 5 and 6, respectively, along with their assignments. The ¹H NMR spectra of the complexes show an upfield shift of the -N-NH-CO signal suggesting coordination of the carbonyl oxygen and/or azomethine nitrogen (23). The signal due to the -N-NH-CO group (C'_{α}) in the ¹³C NMR spectrum of FBzGH



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Table 4.	Infrared S	pectral Data	(cm^{-1})) of the	Com	plexes	of FBz	CH*a
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	Hydrazidic Moiety				
Complex	Amide I	Amide II	$\gamma(C=N)$	$\gamma(NN)$	$\gamma(MO)$
FBzGH	1675 s	1545 s	1570 m	1015 s	-
FBzGH ^{a-}	1720 s	1570 m	1600 m	1005 s	-
[Mn(FBzGH)2Cl(H2O)]Cl	1675 s	1545 s	1570 m	1015 m	360 m
[Cu(FBzGH)2Cl(H2O)]Cl	1670 s	1540 m	1560 m	1010 w	355 ^c m
[Zn(FBzGH) ₂ Cl(H ₂ O)]Cl	1675 s	1545 s	1570 m	1015 m	360 m
[Cd(FBzGH)2Cl(H2O)]Cl	1675 s	1535 s	1570 m	1015 m	360 m
[Hg(FBzGH)2Cl(H2O)]Cl	1675 s	1545 s	1565 m	1015 m	360 m
[Co(FBzGH)2]Cl2·H2O	1655 s	1535 m	1570 m	1015 m	380 m
$[Ni(FBzGH)_2Cl_2]H_2O$	1655 s	1555 m	1575 m	1025 m	380 m
	γ(N	CO ⁻)			
	Amide I	Amide II	$\gamma(C=N)$	$\gamma(NN)$	$\gamma(MO)$
$[Co(FBzG)_2(H_2O)_2]$	1550 s	1305 s	1565 s	1015 s	385 m
$[Ni(FBzG)_2(H_2O)_2]$	1550 s	1305 s	1565 s	1015 s	385 m
$[Cu(FBzG)_2(H_2O)_2]$	1550 s	1300 s	1565 s	1015 s	370 ^c m

s: Strong; m: Medium; w: Weak.

^aThe spectra were recorded as Nujol mulls.

^bIn acetonitrile solution.

^cDoublet.

undergoes a downfield shift in the spectra of the complexes, suggesting coordination of the carbonyl group (24) while that due to the benzamide carbonyl group (C_{α}) does not undergo any remarkable shift in the spectra of the complexes thereby indicating its nonparticipation in bonding. The downfield shift observed in the signals due to the -NCH- carbon also suggests coordination of the azomethine nitrogen (25). The signals due to furane and phenyl rings remain almost unaltered in both the ¹H and ¹³C NMR spectra of the complexes suggesting their noninvolvement in bonding. The ¹¹³Cd NMR spectrum of the Cd(II) complex was recorded in DMSO-d₆ solution and the chemical shift was referenced to external 1.0 M CdSO₄ in H₂O. The resonance signal of the complex was observed as a single line at -347.9 ppm, which is unusually shielded. This shielded nature of this resonance reflects a strongly bound (nonexchanging) Cd²⁺, but one which is "weakly coordinated electronically" (26). "Weakly coordinated electronically" means that the bonding in this complex is more ionic rather than the usual donor-acceptor relation between a ligand and a metal such as cadmium. The highly shielded nature of the complex implies substantially less covalency of the metal-ligand bond resulting in a smaller perturbation from the isolated ion electronic configuration. Nonetheless, the metal ion is far from free. Though weakly covalently ligated, the Cd^{2+} is strongly bound.



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Table 5. ¹H NMR Spectral Data (δ) of FBzGH and the Zn(II), Cd(II), and Hg(II) Complexes^a

			Comp	lexes[M(FBz0	$GH)_2(H_2O)O$	C1]C1
	FBz	GH	Zn(II)	Cd(II)	Ho(II)
Proton(s)	(296 K)	(384 K)	(296 K)	(296 K)	(353 K)	(296 K)
-N-N <u>H</u> CO-	11.70	11.43	11.41	11.43	11.24	11.58
C ₆ H ₅ CON <u>H</u> -	9.07, 8.67	8.60	8.99, 8.60	9.00, 8.80	8.47	8.99, 8.81
-NC <u>H</u> -	8.30	8.17	8.10	8.27	8.13	8.27
-C <u>H</u> 2-	4.53, 4.13	4.40	4.33, 3.98	4.47, 4.10	4.27	4.49, 4.41
Phenyl	8.07 m	8.10 m	7.88 m	8.00 m	7.95	8.04
Protons	7.67 m	7.63 m	7.48 m	7.60 m	7.83	7.68
Furane	7.00	6.93	6.83	6.97	6.90	7.02
Protons	6.73 m	6.73 m	6.55 m	6.71	6.65	6.77

m: Multiplet.

^{*a*}The spectra were recorded in DMSO-d₆.

Thus, the ligand FBzGH was found to behave as a neutral bidentate ligand coordinating through the hydrazidic carbonyl oxygen and the azomethine nitrogen in the adducts while it behaves as an uninegative bidentate ligand bonding through the enolic oxygen of the hydrazidic carbonyl group and azomethine nitrogen. The proposed structures of the complexes are given in Figure 7.

Table 6. Proton-Noise Decoupled ¹³C NMR Spectral Data (ppm) of FBzGH and the Zn(II), Cd(II), and Hg(II) Complexes^a

Carbon	FBzGH		Complex, M(FBzGH) ₂ (H ₂ O)Cl]Cl at 296		
Atoms	296 K	348 K	Zn(II)	Cd(II)	Hg(II)
$\overline{C'_{\alpha}}$	169.25	_	170.22	170.17	170.26
Cα	166.87,166.12	166.43	166.75, 166.30	166.65, 165.67	166.26
$-CH_2-$	40.77	40.42	41.28	40.45	41.34
-N <u>C</u> H-	143.95	144.44	144.92	144.98	144.90
C(1)	131.43	130.84	131.74	131.38	131.43
C(2)	127.32	127.86	128.35	128.35	128.26
C(3)	126.34	126.94	127.35	127.32	127.15
C(4)	132.68	133.98	133.71	134.03	133.80
C(2')	148.23	149.15	149.15	149.15	149.50
C(3')	112.26	112.36	113.29	113.56	113.20
C(4')	111.12	111.67	112.15	112.15	111.93
C(5′)	136.82	-	136.74	136.69	139.03

^aThe spectra were recorded in DMSO-d₆.



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Figure 7. Proposed structures of the complexes a) M = Mn, Cu, Zn, Cd, Hg; $X = OH_2$; M = Ni; X = Cl, b) M = Co, and c) M = Co, Ni, Cu.

EXPERIMENTAL

Materials

All the chemicals used in the present study were of BDH grade or of equivalent quality. Furfurylidene(*N*-benzoyl)glycine hydrazone was prepared by

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refluxing solutions of *N*-benzoylglycyl hydrazide (5.38 g, \sim 25 mmol in 50 mL of absolute alcohol) and furfural (2.30 g, \sim 40 mmol in 25 mL of absolute alcohol) for 4 h. The brown precipitate obtained on slow cooling of the reaction mixture was filtered, washed repeatedly with cold ethanol, and dried at room temperature. The product obtained on recrystallizing from hot ethanol yielded light brown crystals.

Preparation of the Complexes

Chloroaquobisfurfurylidene(*N*-benzoyl)glycyl Hydrazone]metal(II) Chloride, [M(FBzGH)₂Cl(H₂O)]Cl (M = Mn, Cu, Zn, Cd and Hg), Bis[furfurylidene(*N*-benzoyl)glycyl hydrazone]cobalt(II) Dichloride Hydrate, [Co(FBz-GH)₂]Cl₂ · H₂O, and Dichloro-bis(furfurylidene(*N*-benzoyl)glycyl Hydrazone) nickel(II) Hydrate, [Ni(FBzGH)₂Cl₂] H₂O. These compounds were prepared by mixing together solutions of the metal chloride (0.50 g, 1.0 mmol in 10 mL of ethanol) and FBzGH (1.0 g, 2.0 mmol in 20 mL of acetonitrile) and refluxing the reaction mixture for 1 h. The precipitation was initiated by adding ~20 mL of tetrahydrofuran to the reaction mixture.

Bis(furfurylidene(*N*-benzoyl)glycylhydrazonato)diaquometal(II), [M (FBzG)₂(H₂O)₂] (M = Co, Ni and Cu)]. These compounds were prepared by mixing aqueous solutions of the metal chloride (0.5 g, 1.0 mmol in 10 mL) and the sodium salt of FBzGH (1.0 g, 2.0 mmol in 20 mL) and adjusting the pH of the reaction mixture to \sim 7 by the controlled addition of aqueous NaOH. The precipitates were formed immediately after mixing and were digested on a water bath for 0.5 h.

Preparation of the Solutions for the Determination of the Formation Constants

All of the solutions used in the determination of the formation constants of the complexes were prepared in deionized water. The metal ion–ligand ratio was 1:5 and the ionic strength was adjusted with KNO_3 . The titrations were performed over the pH range 2.5–11.5 with KOH solution. All titration solutions were thermostated at the desired temperatures.

Physical Measurements

The metal ions were determined following the standard procedures (27). Chloride was estimated gravimetrically as AgCl while hydrazine was determined



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volumetrically by titrating against KIO₃ after subjecting the complex to acid hydrolysis. C, H, N were microanalysed. The C, H, N microanalyses were done on a Perkin-Elmer model 240C. Molar conductances were measured at room temperature on a WTW conductivitymeter. The room temperature magnetic susceptibility measurements were carried out using a Cahn–Faraday electrobalance using Hg[Co(NCS)₄] as a calibrant. IR spectra were recorded on a Perkin-Elmer model-783 spectrophotometer while the electronic absorption spectra were recorded on a Cary-14 spectrophotometer in Nujol. The mass spectrum was recorded on a Varian Mat CH-7 mass spectrometer. The pH-metric titrations were performed with a Model 335 Systronic digital pH-meter with a glass electrode (pH range 0-14) and a saturated calomel electrode, which is attached to a thermostat of circular D₈-G Haake Mess Technik. The ESR spectra were obtained at 77 K on a Varian E-line X band ESR spectrometer, using TCNE as a g-marker. The NMR spectra were recorded on a Jeol FX-90Q multinuclear NMR spectrometer.

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