

Synthesis and characterization of the complexes of some transition metals with 2-acetyl pyridine (N-benzoyl) glycylic hydrazone

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Abstract. Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 2-acetyl pyridine (N-benzoyl) glycylic hydrazone(2-ApBzGH) have been synthesized and characterized by elemental analyses, molar conductances, magnetic susceptibility, IR, electronic, ESR, ¹H, ¹³C and ¹¹³Cd NMR spectral and X-ray diffraction studies. IR and NMR data suggest the tridentate nature of the ligand coordinating as a neutral species in the addition complexes and as a uninegative species in the deprotonated complexes. The presence of more than one isomer of the ligand has been established by ¹H NMR spectra of the ligand and complexes recorded over the 298–396 K range. The X-ray powder diffraction patterns of [Cd(2-ApBzGH)Cl]Cl and [Cu(2-ApBzGH)Cl(H₂O)₂]Cl are indexed for orthorhombic and tetragonal crystal systems respectively.

Keywords. Transition complexes; 2-acetylpyridine (N-benzoyl)glycyl hydrazone; isomer; tridentate ligand.

1. Introduction

As a part of our systematic investigation on the 3d and 4f metal complexes of various hydrazides^{1,2} and their schiff bases^{3–7}, we report here the results of our studies on the syntheses and spectral features of complexes of 2-acetylpyridine (N-benzoyl)glycyl hydrazone (2-ApBzGH; figure 1) with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).

2. Experimental

2.1 Materials and methods

All the chemicals used in the present study were of BDH grade or of an equivalent quality. 2-ApBzGH was prepared as reported⁸ and was confirmed by mass, IR, ¹H and ¹³C NMR spectra, m.p. 192–193°C (Lit. 191–193°C). Found: C 64.74; H 5.40; N 18.88; N₂H₄, 10.86%. Calcd: C₁₀H₁₆N₄O₂: C 64.79; H 5.40; N 18.90; N₂H₄, 10.80%.

*For correspondence

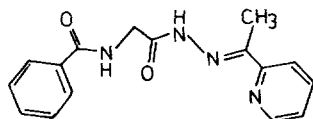


Figure 1. Structure of 2-ApBzGH.

2.2 Preparation and analysis of the complexes

2.2a Adduct complexes: Chloromonokis[2-acetyl pyridine (*N*-benzoyl) glycylic hydrazone] metal(II) chloride, hydrate $[M(2\text{-ApBzGH})Cl]Cl \cdot nH_2O$ [$M = Mn, Zn, Cd, Hg, n = 0$; $M = Co, n = 2$], chloromonokis [2-acetyl pyridine (*N*-benzoyl)glycyl hydrazone] diaqua metal(II) chloride, $[M(2\text{-ApBzGH})Cl(H_2O)_2]Cl$ [$M = Cu, Ni, n = 2$] were prepared by mixing together the ethanolic solutions of the ligand ($\approx 1.0 \text{ mmol}$ in 10 cm^{-3}) and the appropriate metal chloride ($\approx 1.0 \text{ mmol}$ in 10 cm^{-3}) at room temperature. The complexes were either precipitated or precipitation was induced by the addition of $\approx 20 \text{ cm}^3$ ether to the reaction mixture.

2.2b Neutral complexes: Bis[2-acetyl pyridine (*N*-benzoyl)glycyl hydrazonato] metal(II), hydrate $[M(2\text{-ApBzGH-H})_2]$ [$M = Co, Cd$], hydroxomonokis [2-acetyl pyridine (*N*-benzoyl)glycyl hydrazonato] metal(II) $[M(2\text{-ApBzGH-H})(OH)]$ [$M = Mn, Zn, Hg$], hydroxomonokis [2-acetyl pyridine(*N*-benzoyl)glycyl hydrazonato] diaqua metal(II) $[M(2\text{-ApBzGH-H})(OH)(H_2O)_2]$ [$M = Cu, Ni$] were synthesized by mixing an aqueous/ethanolic solution of appropriate metal chloride ($\approx 1.0 \text{ mmol}$ in 20 cm^3) and aqueous solution of the potassium salt of the ligand and adjusting the *pH* of the solution to ~ 7 . The resulting complexes were digested on a water bath for 0.5 h. All the complexes prepared as above were filtered and repeatedly washed with suitable solvents and dried either in a desiccator/air. The complexes were analyzed for metal contents employing standard literature procedures⁹ after destroying the organic matter with aqua regia followed by sulphuric acid. Hydrazine was estimated by titrating against KIO_3 after subjecting the complexes to acid hydrolysis for ~ 4 h. Carbon, hydrogen and nitrogen were microanalyzed.

2.3 Physical measurements

Molar conductance was measured on a WTW conductivity meter in 10^{-3} M DMSO solution. The magnetic susceptibility measurements were carried out at room temperature on a Cahn–Faraday electrobalance. The electronic spectra were recorded on a Cary-14 spectrophotometer and IR spectra on a Perkin–Elmer 783 spectrophotometer in Nujol. ESR spectra were obtained at 77 K on a Varian E-line X band ESR spectrometer using TCNE as a *g* marker. The 1H , ^{13}C and ^{113}Cd NMR spectra were recorded on a Jeol FX-90Q multinuclear NMR spectrometer. The X-ray powder diffraction patterns were taken by Phillips X-ray diffractometer PW 1710 using $CuK\alpha$ radiation.

3. Results and discussion

The analytical results presented in table 1 show that 2-ApBzGH reacts with metal(II) chloride yielding complexes of both 1:1 and 1:2 metal-ligand stoichiometries. It also

Table 1. Analytical data and μ_{eff} values of the complexes of 2-*ApBzGH*.

Complex* M(II)	Colour	m.p. (°C)	Found (calcd) %				Molar conduct (Ω^{-1} $\text{cm}^2\text{mol}^{-1}$)	μ_{eff}^+ (BM)
			M	Cl	N ₂ H ₄	N		
I; Mn	Yellow	277	13.00 (13.01)	16.78 (16.81)	7.32 (7.38)	13.30 (13.26)	41.30	5.70
II; Co	Green	240	12.66 (12.74)	15.30 (15.36)	6.77 (6.92)	12.00 (12.11)	73.55	4.03
III; Zn	White	282	14.91 (15.11)	16.11 (16.41)	7.00 (7.40)	13.05 (12.94)	24.71	Dia.
IV; Cd	White	262	23.33 (23.43)	14.68 (14.80)	6.59 (6.67)	11.46 (11.67)	20.37	Dia.
V; Hg	White	208	35.09 (35.32)	12.50 (12.50)	5.60 (5.63)	9.72 (9.88)	19.62	Dia.
VI; Ni	Light green	240 (<i>d</i>)	12.18 (12.70)	14.66 (15.37)	6.69 (6.92)	11.72 (12.12)	28.29	3.10
VII; Cu	Green	183	13.84 (13.61)	15.30 (15.21)	–	11.22 (11.99)	39.29	2.07
VIII; Mn	Brown	260 (<i>d</i>)	15.86 (14.96)	–	9.10 (9.11)	15.12 (15.25)	–	5.94
IX; Zn	White	282	17.04 (17.26)	–	8.40 (8.45)	14.16 (14.83)	–	Dia.
X; Hg	Greenish yellow	195 (<i>d</i>)	39.10 (39.11)	–	5.92 (6.24)	10.91 (10.92)	–	Dia.
XI; Co	Purple	284	9.69 (9.07)	–	9.50 (9.85)	17.04 (17.24)	–	6.28
XII; Cd	Light yellow	>300	15.34 (15.94)	–	9.01 (9.08)	15.77 (15.89)	–	Dia.
XIII; Ni	Light brown	>300	14.20 (14.39)	–	7.32 (7.84)	13.25 (13.72)	–	3.48
XIV; Cu	Green	220	15.11 (15.43)	–	–	13.51 (13.60)	–	2.08

*I–VII represent complexes with empirical formula $M(2\text{-ApBzGH})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$; VIII–X, $M(2\text{-ApBzGH-H})(\text{OH})$; XI–XII, $M(2\text{-ApBzGH-H})_2$ and XIII, XIV, $M(2\text{-ApBzGH})(\text{OH}) \cdot 2\text{H}_2\text{O}$

[†]dia. – diamagnetic

forms complexes of different compositions depending on the mode of preparation and metal ions. Formation of the adducts is favoured in weakly acidic conditions while the neutral complexes are isolated from mildly basic media. With few exceptions, the complexes are insoluble in water and common organic solvents. All the adducts are soluble in DMSO while the neutral complexes are sparingly soluble or insoluble in the solvent. All the complexes melt or decompose at specific temperatures except the neutral complexes of Ni(II), Mn(II) and Cd(II) which are nonmelting till 300°C. The adducts show 1:1 electrolytic behaviour¹⁰ in DMSO solution. The insufficient solubility of the complexes in suitable solvents precluded the molecular weight determination and growing of single crystal for X-ray crystallographic studies.

3.1 Magnetic measurements and electronic spectra

The room temperature magnetic moments of the paramagnetic complexes are included in table 1 and the electronic spectral bands along with the corresponding assignments are given in table 2. μ_{eff} values of the Mn(II) and Cu(II) complexes are normal for five and

Table 2. Absorption bands and the assigned transitions of the complexes*.

Complex	Band maxima (cm ⁻¹)	Transitions (cm ⁻¹)	B' (cm ⁻¹)
II; Co	6250 (14493, 15038, 16000)	⁴ A ₂ (F) → ⁴ T ₁ (F) → ⁴ T ₁ (P)	659
XI; Co	8620 12346 19608	⁴ T _{1g} (F) → ⁴ A _{2g} (F) → ⁴ T _{2g} (F) → ⁴ T _{1g} (P)	808
VI; Ni	9750 15873 26667	³ A _{2g} (F) → ³ T _{2g} (F) → ³ T _{1g} (F) → ³ T _{1g} (P)	885
XIII; Ni	11830 18182	³ A _{2g} (F) → ³ T _{2g} (F) → ³ T _{1g} (F)	740
VII; Cu	16000	² B _{1g} (D) → ² B _{2g} (D)	—
XIV; Cu	15385	² B _{1g} (D) → ² B _{2g} (D)	—

*The spectra are recorded as nujol mull

one unpaired electrons. The UV spectra of Cu(II) complexes are indicative of distorted octahedral geometry¹¹ around the metal ions. μ_{eff} value and electronic spectral data of Co(II) adduct show metal ion in a tetrahedral geometry¹². μ_{eff} value of the deprotonated Co(II) complex is abnormal. In the absence of variable temperature magnetic moments¹¹, no definite reason can be attributed for this observation. Although the number and positions of the spectral bands of the Co(2-ApBzGH)₂ are inconsistent with an octahedral geometry, the assignment of the spin state in the ground term is of doubtful validity in view of its abnormal μ_{eff} values. An octahedral configuration¹³ for both Ni(II) complexes has been inferred from μ_{eff} values and electronic spectral features. The Racah-parameter values (B') have been calculated for Co(II) and Ni(II) complexes. These values show considerable decrease suggesting a good overlap between metal-ligand orbitals¹⁴.

3.2 IR spectra

The bonding sites of 2-ApBzGH have been assigned by a careful comparison of IR spectra of the complexes with that of 2-ApBzGH (table 3). The Nujol mull IR spectrum of 2-ApBzGH shows bands at 1690, 1545 and 1310 cm⁻¹ and 1630, 1535 and 1305 cm⁻¹ which may be assigned to amide I, II and III modes of the hydrazide and benzamide moieties⁸ respectively. The positions of the amide I, II and III bands arising from the benzamide >C=O group remain almost unaltered in the spectra of all the complexes as compared to those of the metal-free ligand, suggesting non-involvement of the above group in bonding. However, the corresponding amide bands of the hydrazide >C=O group appear in the 1675–1640, 1515–1505 and 1335–1325 cm⁻¹ regions in the spectra of the adducts indicating its involvement in coordination¹⁵. These amide bands disappear from the spectra of all the neutral complexes and a sharp band diagnostic of the >C=N–N=C< group appears at 1600–1590 cm⁻¹ indicating destruction of hydrazide >C=O through amide↔imidol tautomerism and subsequent coordination through the imidol oxygen. The appearance of new peaks characteristic of (NCO⁻) in the 1515–1500 and 1335–1330 cm⁻¹ regions in the spectra of the neutral complexes further supports the coordination of the imidol group¹⁶. Coordination through azomethine nitrogen¹⁷ is suggested on the basis of the observed hypsochromic shift (15–50 cm⁻¹) of the (N–N) and bathochromic shift

Table 3. IR spectral data (cm^{-1}) of the complexes of 2-ApBzGH*.

Complex M(II)	Hydrazidic moiety			$\gamma(>\text{C}=\text{N}-\text{N}=\text{C}<)$	$\gamma(\text{C}=\text{N})$	$\gamma(\text{NN})$	$\gamma(\text{MO})$
	Amide I	II	III				
2-ApBzGH	1690 (<i>vs</i>)	1545 (<i>s</i>)	1310 (<i>s</i>)	–	1585 (<i>s</i>)	1045 (<i>m</i>)	–
I; Mn	1660 (<i>vs</i>)	1515 (<i>s</i>)	1330 (<i>s</i>)	–	1570 (<i>s</i>)	1070 (<i>s</i>)	380 (<i>m</i>)
II; Co	1640 (<i>vs</i>)	1505 (<i>s</i>)	1330 (<i>m</i>)	–	1570 (<i>s</i>)	1075 (<i>s</i>)	385 (<i>w</i>)
III; Zn	1670 (<i>vs</i>)	1515 (<i>s</i>)	1335 (<i>m</i>)	–	1565 (<i>s</i>)	1080 (<i>s</i>)	380 (<i>m</i>)
IV; Cd	1660 (<i>s</i>)	1510 (<i>s</i>)	1325 (<i>m</i>)	–	1570 (<i>m</i>)	1065 (<i>s</i>)	400 (<i>w</i>)
V; Hg	1675 (<i>vs</i>)	1510 (<i>vs</i>)	–	–	1570 (<i>w</i>)	1070 (<i>vs</i>)	360 (<i>w</i>)
VI; Ni	1660 (<i>s</i>)	1515 (<i>m</i>)	1330 (<i>m</i>)	–	1565 (<i>m</i>)	1075 (<i>m</i>)	350 (<i>w</i>)
VII; Cu	1660 (<i>vs</i>)	1505 (<i>s</i>)	1330 (<i>m</i>)	–	1545 (<i>s</i>)	1075 (<i>m</i>)	340 (<i>w</i>)
	$\gamma(\text{NCO}^-)$						
VIII; Mn	1510 (<i>s</i>),	1330 (<i>s</i>)	1595 (<i>m</i>)	1565 (<i>s</i>)	1090 (<i>m</i>)	370 (<i>m</i>)	
IX; Zn	1510 (<i>m</i>),	1335 (<i>s</i>)	1595 (<i>m</i>)	1565 (<i>m</i>)	1060 (<i>w</i>)	390 (<i>m</i>)	
X; Hg	1515 (<i>s</i>),	1330 (<i>s</i>)	1590 (<i>s</i>)	1565 (<i>s</i>)	1095 (<i>s</i>)	360 (<i>m</i>)	
XI; Co	1500 (<i>m</i>),	1335 (<i>vs</i>)	1595 (<i>s</i>)	1550 (<i>m</i>)	1060 (<i>m</i>)	385 (<i>m</i>)	
XII; Cd	1510 (<i>s</i>),	1335 (<i>s</i>)	1590 (<i>s</i>)	1565 (<i>m</i>)	1075 (<i>m</i>)	350 (<i>w</i>)	
XIII; Ni	1515 (<i>s</i>),	1335 (<i>m</i>)	1595 (<i>s</i>)	1565 (<i>m</i>)	1060 (<i>m</i>)	370 (<i>w</i>)	
XIV; Cu	1515 (<i>s</i>),	1335 (<i>s</i>)	1600 (<i>s</i>)	1565 (<i>m</i>)	1060 (<i>m</i>)	380 (<i>w</i>)	

*The spectra are recorded as nujol mull

vs – very strong; *s* – strong; *m* – medium; *w* – weak

(15–40 cm^{-1}) of the (C=N) bands in the spectra of all the complexes as compared to their appearance at 1045 and 1585 cm^{-1} respectively in the spectrum of the ligand. The hypsochromic shift observed in the pyridine ring breathing (10–15 cm^{-1}), in-plane (30–35 cm^{-1}) and out-of-plane (40–50 cm^{-1}) deformation modes indicates coordination of the pyridine ring nitrogen¹⁸. Appearance of a new band in the 1150–1145 cm^{-1} in the spectra of the neutral complexes attributable to the M-OH bending indicates the formation of M-OH bond in the complexes¹⁹. The bands appearing in the 400–340, 380–315 and 290–270 cm^{-1} regions in the spectra of the complexes may be tentatively assigned to the (M-O), (M-N) and (M-Cl) modes²⁰.

3.3 ESR spectra

The ESR spectra of the Cu(II) complexes are isotropic at room temperature but show anisotropic features at LNT and are characteristic of axial symmetry. The g_{\parallel} and g_{\perp} values are 2.281 and 2.057 for $[\text{Cu}(2\text{-ApBzGH})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}$ and 2.256 and 2.071 for $[\text{Cu}(2\text{-ApBzGH-H})(\text{OH})(\text{H}_2\text{O})]$ complexes, respectively. The trend $g_{\parallel} > g_{\perp} > g_e$ indicates tetragonal elongation along z-axis and presence of unpaired electron in $b_{1g}(d_{x^2-y^2})$ orbital²¹. The in-plane σ -bonding parameter (α^2) calculated for these Cu(II) complexes, 0.69 and 0.79 predicts a predominant covalent in-plane bonding²².

3.4 ^1H , ^{13}C and ^{113}Cd NMR spectra

^1H and ^{13}C NMR spectral data of 2-ApBzGH and the Zn(II), Cd(II) and Hg(II) complexes were recorded in DMSO- d_6 and the spectral bands along with the assignments are given in tables 4 and 5 respectively. Although ^1H NMR spectrum of the ligand (figure 2) shows

Table 4. ^1H NMR spectral data (δ) of 2-ApBzGH and its $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ and $[\text{Cd}(2\text{-ApBzGH-H})_2]$ complexes.

Proton(s)	2-ApBzGH (296 K)	[Cd(2-ApBzGH)Cl]Cl		[Cd(2-ApBzGH-H) ₂] (296 K)
		(296 K)	(343 K)	
Hydrazidic-NH-	10.85 (<i>s</i>)	11.42 (<i>s</i>), 12.48 (<i>s</i>)	11.13 (<i>s</i>)	-
Benzamide-NH-	8.71 (<i>s</i>)	8.88 (<i>t</i>), 9.21 (<i>t</i>)	8.93 (<i>t</i>)	8.62 (<i>t</i>)
-CH ₂ -	4.52 (<i>d</i>)	4.41 (<i>d</i>), 4.58 (<i>d</i>)	4.50 (<i>d</i>)	4.01 (<i>d</i>)
-CH ₃ -	2.38 (<i>s</i>)	2.41 (<i>s</i>), 2.62 (<i>s</i>)	2.50 (<i>s</i>)	2.50 (<i>s</i>)
Ring protons	8.57 (<i>d</i>)	8.78 (<i>d</i>)	8.80 (<i>d</i>)	7.99 (<i>m</i>)
	7.91 (<i>m</i>)	8.17 (<i>m</i>)	8.21 (<i>d</i>)	7.54 (<i>b</i>)
	87.52 (<i>m</i>)	87.93 (<i>m</i>)	88.10 (<i>t</i>)	-
	-	87.61 (<i>d</i>)	87.67 (<i>d</i>)	-

s - singlet; *d* - doublet; *t* - triplet; *m* - multiplet

Table 5. Proton-noise decoupled ^{13}C NMR spectral data (ppm) of 2-ApBzGH and the $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ complex.

Carbon atom	2-ApBzGH (296 K)	[Cd(2-ApBzGH)Cl]Cl	
		(296 K)	(343 K)
Hydrazidic >C=O	170.7	171.1, 171.4	169.6
Benzamide >C=O	167.0	166.9	166.9
-H ₃ C	11.8	11.3, 13.2	-
-H ₂ C-	41.3	-	-
-NC-	153.0	150.5 (<i>d</i>)	150.9
C(1)	131.3	131.4	131.4
C(2)	128.2	128.6	128.9
C(3)	127.3	127.9	126.9
C(4)	134.1	133.3	-
C(2')	154.9	154.4	-
C(3')	123.9	123.5	123.8
C(4')	135.5	136.2	135.9
C(5')	120.0	120.0	121.6
C(6')	148.5	149.2 (<i>d</i>)	-

d - doublet

that more than one isomer exists at room temperature, the extremely weak peaks due to the second isomer indicate its negligible contribution at 296 K to the overall structure of 2-ApBzGH. Stabilisation of the second isomer after complexation is being suggested by the two sets of signals for hydrazide-NH-(δ , 11.42 *s*, 12.48 *s*), benzamide-NH-(δ , 8.88 *t*, 9.21 *t*), CH₂-(δ , 4.41 *d*, 4.58 *d*), -CH₃-(δ , 2.41 *s*, 2.62 *s*) in the ^1H NMR spectrum of $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$. These isomers are usually non-separable due to the relatively low barrier to rotation²³. However as the temperature is raised, the coalescence of the peaks occur showing stabilisation of one of the conformers at a higher temperature. Figure 3 shows the signals due to hydrazidic -NH- and -CH₂- groups in the ^1H NMR spectrum of $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ as a function of temperature. The hydrazidic -NH- signal appearing at δ 10.85 in the spectrum of 2-ApBzGH indicates a downfield shift at δ 12.52, δ 12.48 and

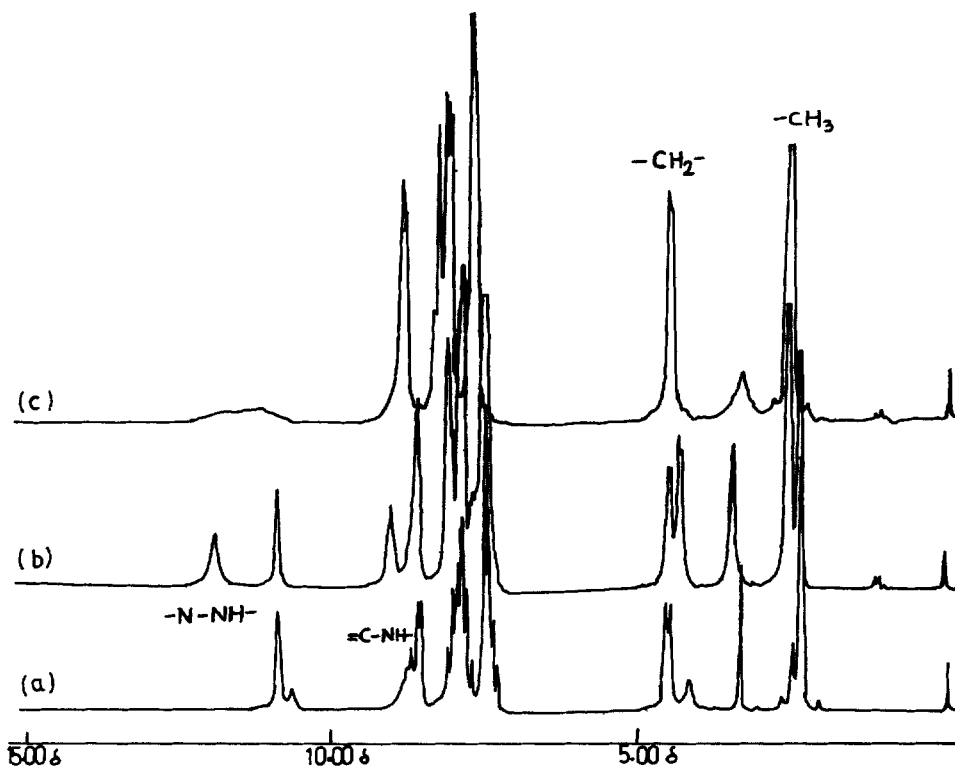


Figure 2. ^1H NMR spectra of (a) 2-ApBzGH at 296 K; (b) $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ at 296 K and $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ at 343 K.

δ 11.81 for Zn(II), Cd(II) and Hg(II) adducts respectively suggesting coordination of 2-ApBzGH through hydrazidic $>\text{C}=\text{O}$ and azomethine nitrogen²⁴. In the ^1H NMR spectrum of the $[\text{Cd}(2\text{-ApBzGH}\text{-H}_2)]$ complex, the signal due to imino-proton of the hydrazide moiety disappears thereby confirming deprotonation of the imino proton and bonding through imidol oxygen in the neutral complexes. The signals due to methyl and methylene protons do not show any significant shift in the spectrum of $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$.

The ^{13}C NMR spectra (figure 4) of the complexes also show the splitting features of hydrazide $>\text{C}=\text{O}$ and $-\text{CH}_3$ signals associated with the presence of more than one isomer of 2-ApBzGH in the complexes at 296 K. Coordination through hydrazidic $>\text{C}=\text{O}$ and azomethine nitrogen^{25,26} have been deduced from the shift of the $>\text{C}=\text{O}$ and $-\text{NC}-$ resonance signals in the complexes (2-ApBzGH 170.7, 153.0 ppm; Zn(II) 171.7, 150.8; Cd(II) 171.4, 150.5 ppm and Hg(II) 171.7, 150.8 ppm). The signals due to benzamide $>\text{C}=\text{O}$ and benzene ring carbons show no remarkable shift. Bonding through pyridine ring nitrogen²⁶ is also shown by the downfield shift (1.00–1.65 ppm) in the C(5') signal in the spectra of the complexes.

^{113}Cd NMR spectrum of $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ was recorded in DMSO-d_6 and the chemical shift was referenced to external 1.0 M CdSO_4 in H_2O . The resonance signal of the complex was observed as a single line at -347.9 ppm, which is unusually shielded.

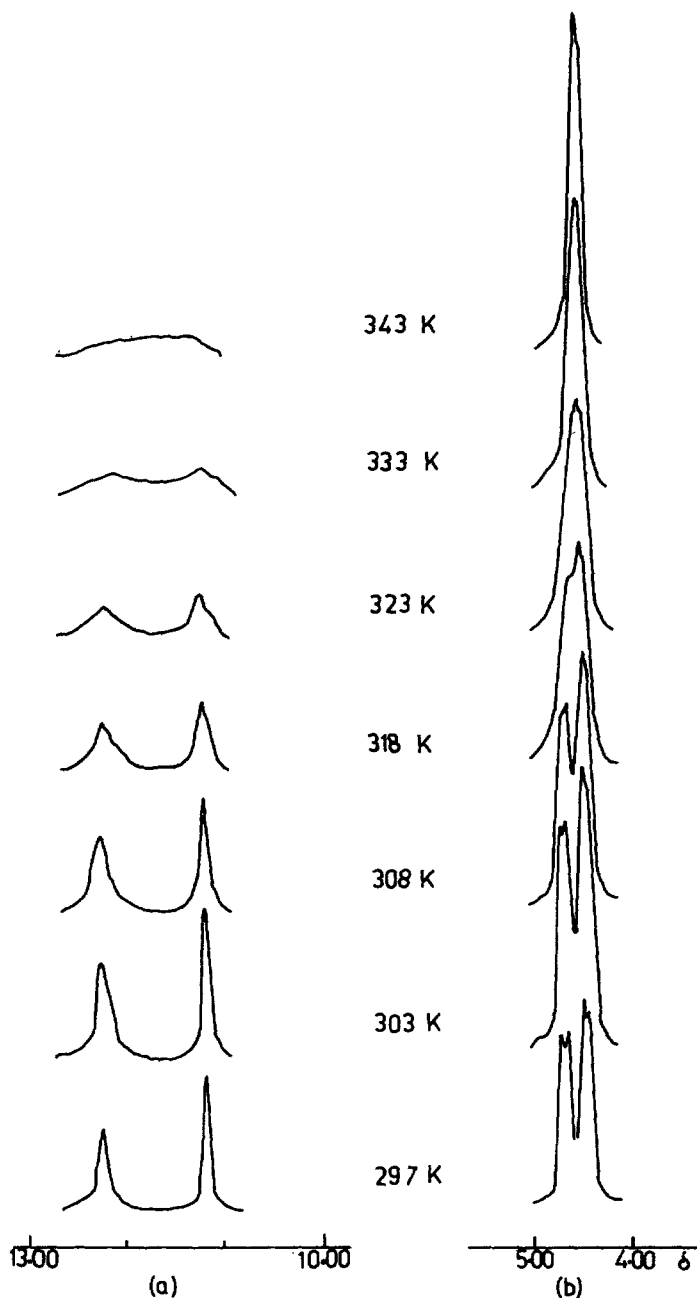


Figure 3. ^1H NMR spectral peaks of $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ as a function of temperature (a) Hydrazidic-NH- and (b) -CH₂- signals.

The shielded nature of this resonance reflects a strongly bound (nonexchanging) cadmium ion, but one which is electronically weakly coordinated i.e., the bonding in this system is more ionic rather than the usual donor-acceptor relation between a ligand and a metal

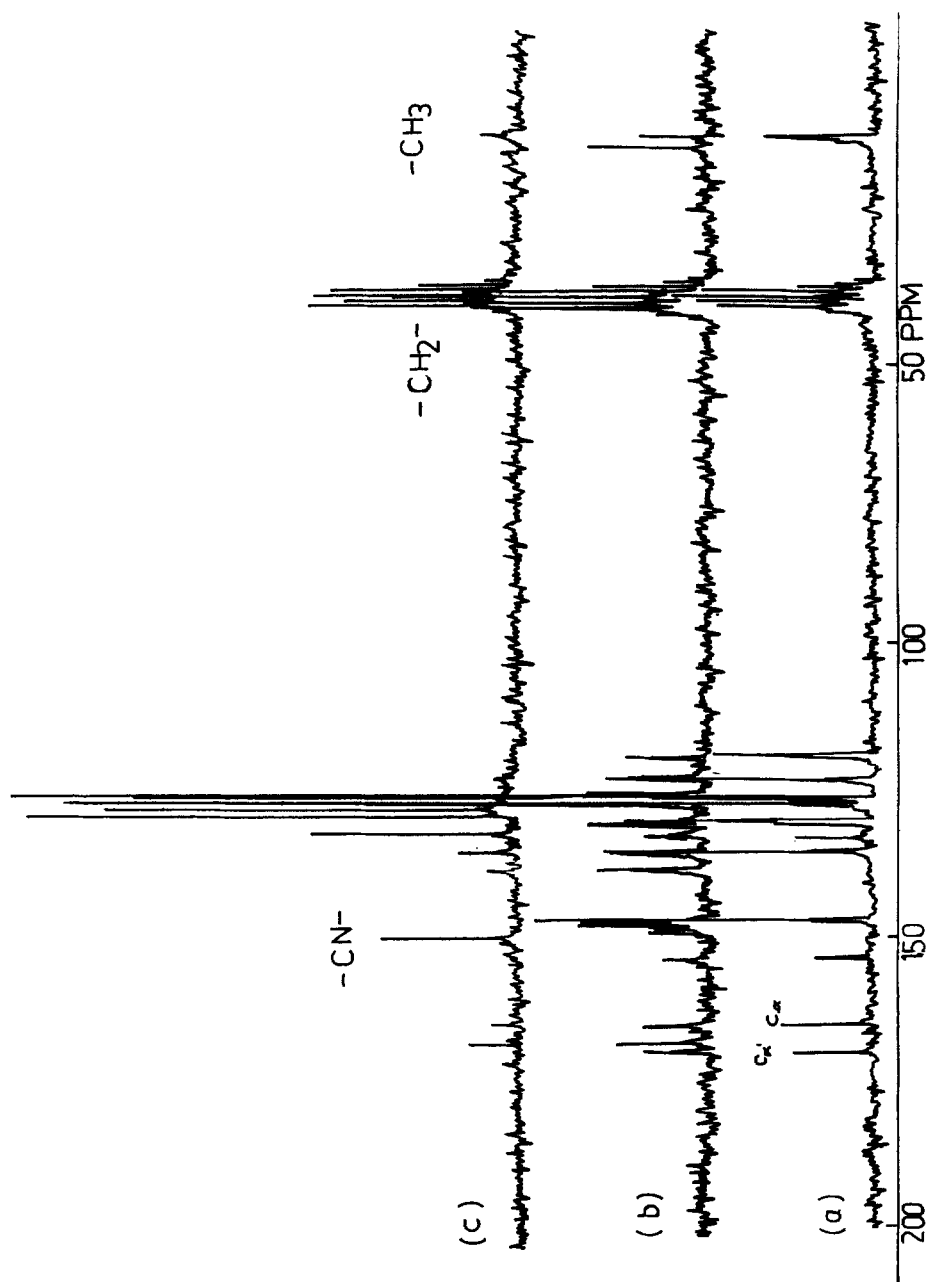


Figure 4. ^{13}C NMR spectra of (a) 2-ApBzGH at 296 K; (b) $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ at 296 K and (c) $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ at 343 K; C_α signal is for hydrazidic $>\text{C}=\text{O}$ and C_α for benzamide $>\text{C}=\text{O}$.

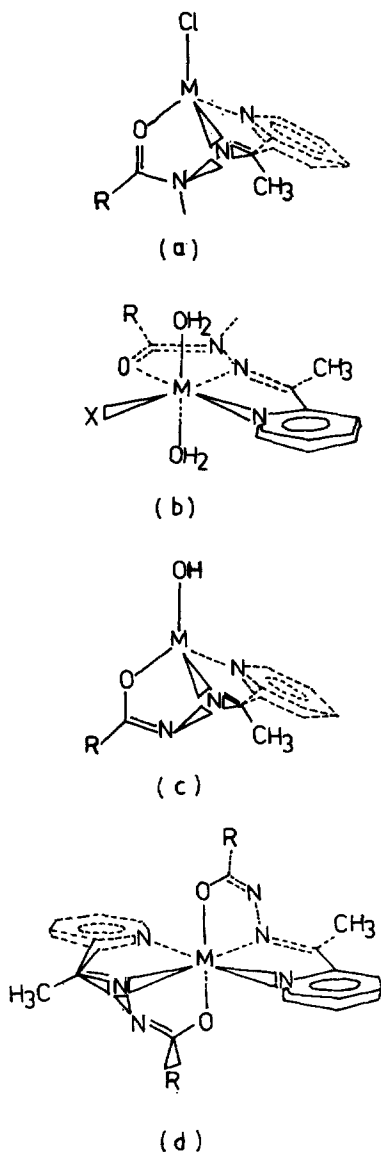


Figure 5. Proposed structures of the complexes (a) $M = \text{Mn, Co, Zn, Cd, Hg}$; (b) $M = \text{Ni, Cu}$; $X = \text{Cl/OH}$; (c) $M = \text{Mn, Zn, Hg}$ and (d) $M = \text{Co, Cd}$.

such as cadmium²⁷. This highly shielded chemical shift value is also expected to have orthogonal environment²⁸.

3.5 X-ray diffraction studies

The X-ray powder diffraction patterns of the complexes have been indexed successively²⁹. The indexing of the pattern yields the lattice constants, $a = 10.14 \text{ \AA}$; $b = 6.01 \text{ \AA}$; $c = 5.65 \text{ \AA}$ indicating an orthorhombic system for $[\text{Cd}(2\text{-ApBzGH})\text{Cl}]\text{Cl}$ and

$a = b = 12.39 \text{ \AA}$; $c = 19.25 \text{ \AA}$ for $[\text{Cu}(2\text{-ApBzGH})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}$ showing its crystal to be tetragonal.

4. Conclusion

The analytical data of the complexes suggest that 2-ApBzGH can form complexes in both 1:1 and 1:2 ratio. The electrical conductance shows 1:1 electrolytic nature of the adducts. IR, ^1H and ^{13}C NMR spectra suggest tridentate behaviour of 2-ApBzGH coordinating through hydrazidic $>\text{C}=\text{O}$, azomethine nitrogen and ring nitrogen as a neutral ligand in the adducts and uninegative ligand in the deprotonated complexes through keto-enol tautomerism. More ionic bonding in the complexes is being suggested by the highly shielded ^{113}Cd chemical shift value. Figure 5 shows the tentative structures proposed for the complexes.

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