
PHYSICOCHEMICAL STUDIES ON SOME HYDRAZONE COMPLEXES

HAMDY A. HAMMAD

Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo 11884, Egypt

Abstract

Some hydrazones and their complexes were prepared in order to study their molecular structures. The hydrazones were prepared by condensing p-aminobenzoic acid hydrazide with some aldehydes. The of Cu(II), Ni(II) and Co(II) were prepared and characterized by elemental analysis, magnetic, electronic and IR methods.

Introduction

Acid hydrazides and hydrazones received a considerable attention as antibacterial substances⁽¹⁾, catalytic⁽²⁾ and versatile chelating agents^(3,4). A survey of literature reveals that a considerable amount of work on their transition metal complexes have been carried out⁽⁵⁻¹⁶⁾.

The present paper reports the results of synthesis, characterization and of Cu(II), Ni(II) and Co(II) acetate with P-aminobenzoyl salicyl hydrazone (ABSH) and P-aminobenzoyl naphthyl hydrazone (ABNH), in order to investigate their molecular structures.

Experimental

All chemicals used are of pure grade p-amino-benzoic acid hydrazide was prepared by previous method⁽¹⁷⁾. ABSH and ABNH were prepared by condensing p-aminobenzoic acid hydrazide with salicylaldehyde and o-hydroxynaphthaldehyde. The products were crystallized from ethanol. Metal complexes were prepared by refluxing aqueous ethanolic solution of the ligand and metal acetate in the appropriate ratio (1:1) for two hours. After cooling the complexes were filtered off, washed with ethanol and dried in vacuo. The complexes were chemically analysed for C, H, N and metals and the results are given in Table (1). Magnetic susceptibility measurements were obtained at room temperature using Gouy method. Electronic spectra were recorded as NaCl disks, where small amount of complexes were mixed with 0.1 gm NaCl. The electronic spectra were recorded using Perkin-Elmer λ_{20} spectrophotometer. Infrared spectra of the complexes were measured using Perkin-Elmer Spectrum 1 spectrophotometer.

Results and Discussion

The prepared complexes were analysed and their elemental analysis (Table 1) indicate that these complexes possess 1:1 (metal : ligand) stoichiometry. The IR spectra are listed in Table (II). The IR spectra of the ligands indicate the presence of amide I ($\nu\text{C}=\text{O}$), azomethine ($\nu\text{C}=\text{N}$), amide II (δNH), occurring at about 1710, 1620 and 1600 cm^{-1} respectively, while δOH and νCO bands appeared at 1350 and 1170 cm^{-1} . The comparison between the spectra of the ligands and the spectra of complexes indicate that $\nu\text{C}=\text{O}$ is shifted to higher frequency in the spectra of complexes. It is thus believed that $\text{C}=\text{O}$ group does not participate in complex formation. The inspection of the spectra of complexes reveals remarkable shifts to lower frequency in the azomethine, amide II and νCO bands upon complexation. Furthermore, the absorption bands at about 1355 cm^{-1} , attributable to δOH in the free ligands, disappeared in the spectra of these complexes. These changes in the group vibrations of the azomethine and CO absorption, beside the disappearance of δOH mode are consistent with the coordination through the phenolic oxygen and azomethine nitrogen. The changes in the position and intensity of the broad absorption bands at about 3400 cm^{-1} , in addition to weak absorption peaks at about 780 and 510 cm^{-1} in the IR spectra of these complexes, indicate the presence of coordinated water molecules⁽¹⁸⁾. In addition the spectra of complexes contain strong absorption bands at about 1600 and 1540 cm^{-1} , characteristic of the coordinated acetate ion⁽¹⁹⁾.

Magnetic susceptibility measurements showed that all complexes are paramagnetic. The obtained values of the effective magnetic moment (μ_{eff}) indicate that the complexes have octahedral symmetry⁽²⁰⁾. The data are listed in Table (3). The electronic spectra of the ligands and their complexes were recorded as NaCl disks. The colour and electronic spectral data for complexes are given in Table (3). The data indicated that these complexes are octahedrally coordinated⁽²¹⁾ in agreement with the conclusions from the magnetic susceptibility measurements. On the basis of preceding discussion, the suggested structure of the metal chelates under investigation is shown in Fig. (1).

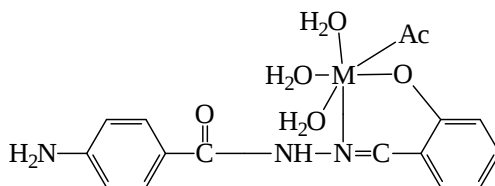


Figure (1): Proposed structure for metal-chelates.

Table (1): Physical and Analytical data of ABSH, ABNH and their complexes.

Compound	m.p.	M wt	Molecular Formula	Chemical Analysis Calculated/Found			
				C	H	N	M
ABSH	82	254	$C_{14}H_{12}N_3O_2$	66.1	4.7	16.5	—
				65.8	4.4	16.4	—
Cu^{2+} -ABSH	162	429	$C_{14}H_{11}N_3O_2CuAc3H_2O$	44.7	4.6	9.7	14.6
				44.5	4.2	9.3	14.3
Ni^{2+} -ABSH	<300	424	$C_{14}H_{11}N_3O_2NiAc3H_2O$	45.2	4.7	9.9	13.6
				44.0	4.5	9.7	13.2
Co^{2+} -ABSH	270	424	$C_{14}H_{11}N_3O_2CoAc3H_2O$	45.2	4.7	9.9	13.6
				44.1	4.6	9.6	13.4
ABNH	130	304	$C_{18}H_{14}N_3O_2$	71.0	4.6	13.8	—
				70.8	4.3	13.6	—
Cu^{2+} -ABNH	208	479	$C_{18}H_{13}N_3O_2CuAc3H_2O$	50.1	4.5	8.7	13.1
				49.7	4.3	8.5	12.9
Ni^{2+} -ABNH	<300	474	$C_{18}H_{13}N_3O_2NiAc3H_2O$	50.6	4.6	8.8	12.2
				50.2	4.5	8.6	12.0
Co^{2+} -ABNH	244	474	$C_{18}H_{13}N_3O_2CoAc3H_2O$	50.6	4.6	8.8	12.2
				50.3	4.4	8.5	11.9

Table (2): Infrared characteristic frequency vibrations of ABSH, ABNH and their complexes.

	ABSH	Cu^{2+} - ABSH	Ni^{2+} - ABSH	Co^{2+} - ABSH	ABNH	Cu^{2+} - ABNH	Ni^{2+} - ABNH	Co^{2+} - ABNH
νOH	3400 w.br.	3422 m.br.	3450 m.br. 3376	3392 s.br.	33903m.br.	3464 m.br.	3400 m.br.	3470 m.br.
$\nu NH + NH_2$	3060 w.br.	3058 w.br.	3025 w.br.	3025 w.br.	3050 w.br.	3048 w.br.	3050 w.br.	3040 w.br.
amid I ($\nu = 0$)	1706 s	1712 vs	1708 vs	1714 m	1710 s	1716 s	1714 vs	1716 s
$\nu C=O$ (acetate)	—	1602 vs	1602 vs	1602 vs	—	1598 s	1598 s	1600 m
δNH	1600 s	1588 vs	1575 sh	1575 sh	1594 s	1578 s	1582 vs	1568 s
$\nu C=O$ (acetate)	—	1536 vs	1542 s	1542 vs	—	1540 vs	1540 vs	1532 s
δOH	1360 m	—	—	—	1350 m	—	—	—
νCO	1166 s	1152 vs	1152 vs	1152	1172 m	1164 s	1162 s	1164 s
CH_3 acetate	—	1330 m	1340 w	1334	—	1344 m	1344 s	1340 sh
H_2O	—	796 w	800 sh	792	—	776 w	776 w	770 m
H_2O	—	482 w	516 w	490	—	526 w	532 w	502 m
$\nu M-O$	—	458 w	545 w	458	—	498 w	448 m	542 w

Table (3a): Colour and electronic spectral data of ABSH and ABNH.

Compound	Colour	Peak position cm^{-1}	Assignment
ABSH	Light yellow	20,000 & 27,397	$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$
ABNH	Orange	19,607 & 22,222 & 31,250	

Table (3b): Colour and electronic spectral data of copper complexes.

Compound	Colour	μ_{eff}	${}^2T_{2g} \leftarrow {}^2E_g \text{ cm}^{-1}$
Cu^{2+} -ABSH	Dark brown	1.89	13,333
Cu^{2+} -ABNH	Brown	1.87	13,227

Table (3c): Colour, μ_{eff} and electronic spectral data of nickel complexes.

Compound	Colour	μ_{eff} BM	${}^3T_{1g} \leftarrow {}^3A_{2g}$	${}^3T_{1g(p)} \leftarrow {}^3A_{2g}$
Ni^{2+} -ABSH	Green	3.25	18,867	24,396
Ni^{2+} -ABNH	Green	3.15	15,384	27,027

Table (3d): Colour, μ_{eff} and electronic spectral data of cobalt complexes.

Compound	Colour	μ_{eff}	${}^4T_{2g} \leftarrow {}^4T_{1g}$	${}^4T_{1g(p)} \leftarrow {}^4T_{1g}$
Co^{2+} -ABSH	Brown	4.87	18,348	24,641
Co^{2+} -ABNH	Reddish brown	4.62	16,666	23,809

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