

# Synthesis and Physicochemical Investigation of Metal Complexes with Hydrazone and Isonicotinoylhydrazone of Acetoacetanilide

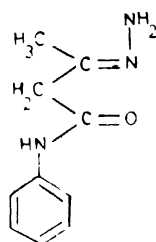
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The chemistry of hydrazones and their metal complexes has created great interest and enthusiasm among chemists because of their analytical, industrial and pharmacological importances. A search through literature revealed that most of the work reported on hydrazones have centered around those derived from simple aldehydes and ketones<sup>1,2</sup> and much less work has been reported on those of  $\beta$ -diketo derivatives<sup>3</sup>. These ligand systems which can behave as bidentate or tridentate towards metal ions are shown to have immense antitumour activity<sup>3,4</sup>. They have also been used in the synthesis of biologically important pyrazolones<sup>5</sup>. With this

analytical data shows that the complexes have the stoichiometry as presented in Table 1.

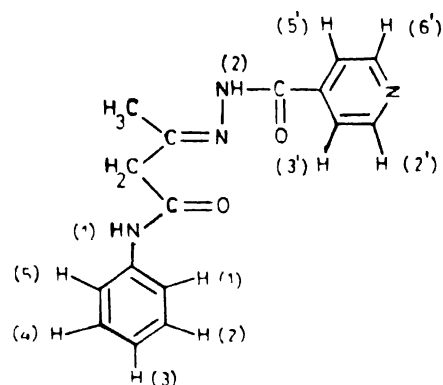


1a (AaH)

in view, hydrazone (AaH) and isonicotinoyl hydrazone (AaINH<sub>2</sub>) of acetoacetanilide (1a and 1b) have been chosen to investigate in terms of their donor characteristics towards several typical transition metal ions.

## Results and Discussion

All the complexes are coloured, non-hygroscopic amorphous powder and air- and photostable. They are sparingly soluble in alcoholic solvents but are appreciably soluble in DMSO. The



1b (AaINH<sub>2</sub>)

[Co(AaIN)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> registers a magnetic moment of 4.16 B.M. It is slightly lower than the value expected for a high-spin Co<sup>II</sup> complex with enough magnetic dilution. The pink colour of the complex along with the electronic spectral data eliminate the possibility of having a tetrahedral geometry for it. A dibasic tridentate ligand along with two water molecules coordinated to Co<sup>II</sup> may facilitate enough magnetic exchange by the way of association through electron-rich centers of the neighbouring complex molecules (i.e. the oxygen atoms). It can also be assumed that the individual molecule may have distorted octahedral geometry<sup>6,7</sup>. The  $\mu_{\text{eff}}$  values of 3.86 and 3.54 B.M. respectively, for Ni(Aa)<sub>2</sub> and [Ni(AaINH)<sub>2</sub>] correspond to tetrahedral Ni<sup>II</sup> ion<sup>8</sup>. The Cu<sup>II</sup> complexes, [Cu(Aa)<sub>2</sub>] and [Cu(AaIN)<sub>2</sub>] register moments of 1.80 and 1.57 B.M. respectively, The value lower than the spin-

only value for the  $\text{Cu}^{\text{II}}$  in the latter case may be attributed to the antiferromagnetic exchange interactions between neighbouring metal ions in  $[\text{Cu}(\text{AaIn})_n]$ .

TABLE 1—ANALYTICAL DATA OF THE COMPLEXES

Compd./ (colour)	Analysis : Found/(Calcd.)			
	C	H	N	M
AaH	62.19 (62.82)	6.16 (6.28)	21.87 (21.98)	—
$[\text{Ni}(\text{Aa})_2]$ (Light blue)	53.18 (54.70)	5.18 (5.47)	18.92 (19.14)	12.95 (13.38)
$[\text{Cu}(\text{Aa})_2]$ (Brown)	54.49 (54.11)	5.16 (5.39)	18.63 (18.93)	14.67 (14.32)
$\text{AaInH}_2$	61.81 (61.73)	5.81 (5.46)	18.68 (18.91)	—
$[\text{Co}(\text{AaIn}(\text{H}_2\text{O})_2)_n]$ (Pink)	48.13 (49.75)	3.81 (4.40)	15.37 (15.09)	15.78 (15.88)
$[\text{Ni}(\text{AaInH}_2)]$ (Bluish green)	56.10 (56.57)	4.80 (4.42)	17.13 (17.16)	9.13 (9.04)
$[\text{Cu}(\text{AaIn})_n]$ (Green)	51.67 (51.53)	4.81 (4.02)	15.63 (15.58)	17.67 (17.77)
$[\text{Zn}(\text{AaIn}(\text{H}_2\text{O})_2)_n]$	49.36 (48.93)	5.01 (4.33)	14.63 (14.18)	16.59 (17.32)

Single line esr spectra are observed with the isotropic  $g$ -values of 2.09 and 2.28 respectively, for  $[\text{Cu}(\text{Aa})_2]$  and  $[\text{Cu}(\text{AaIn})_n]$ , which indicate considerable covalent character of the metal-ligand bond in the present complexes.

$[\text{Co}(\text{AaIn}(\text{H}_2\text{O})_2)_n]$  shows two bands of medium intensity at 21 640 and 12 200  $\text{cm}^{-1}$ , assigned respectively to the transitions,  ${}^4T_{1g} \rightarrow {}^4T_{1g}$  ( $P$ ) ( $\nu_3$ ) and  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  ( $F$ ) ( $\nu_1$ ) of an octahedral  $\text{Co}^{\text{II}}$  complex. The transition,  ${}^4T_{1g} \rightarrow {}^4A_{2g}$  ( $\nu_2$ ) is a two-electron process and is normally weak. Here the ratio,  $\nu_3/\nu_1 = 1.77$ , which is lower than that expected for an octahedral  $\text{Co}^{\text{II}}$  complex<sup>8</sup> (1.95–2.48), suggests certain amount of distortion from true octahedral geometry. This is supplemented by its low magnetic moment value.  $[\text{Ni}(\text{Aa})_2]$  and  $[\text{Ni}(\text{AaInH}_2)]$  register spectral bands at 27 090–26 800 and 16 700–15 600  $\text{cm}^{-1}$ . The later band may be attributed to the transition,  ${}^3T_1 \rightarrow {}^3T_1$  ( $P$ ) typical of tetrahedral geometry. For  $\text{Cu}(\text{Aa})_2$  and  $[\text{Cu}(\text{AaIn})_n]$  two bands at about 22 580 and 15 300  $\text{cm}^{-1}$  correspond respectively, to the transitions,

${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$ , of square-planar  $\text{Cu}^{\text{II}}$  complex<sup>9</sup>.

The highest frequency bands in the spectrum of AaH, observed at 3 450, 3 300 and 3 230  $\text{cm}^{-1}$  may be assigned to the asymmetric and symmetric  $\nu_{\text{NH}}$  of the terminal  $\text{NH}_2^{10}$ . In the spectra of its metal chelates these bands are retained almost in the same region. In the spectrum of  $\text{AaInH}_2$  the bands at 3 210 and 3 150  $\text{cm}^{-1}$  may be attributed to the symmetric  $\nu_{\text{NH}}$  of the imino groups. In the spectra of all the  $\text{AaInH}_2$  complexes, except that of  $\text{Ni}^{\text{II}}$ , the band at 3 210  $\text{cm}^{-1}$  is not observed. It may be as a consequence of enolisation of  $\text{N-NH-C=O}$  to  $\text{N=N-C-OH}$  and subsequent coordination through deprotonated oxygen. However, in the spectrum of the  $\text{Ni}^{\text{II}}$  complex, the imino and associated vibrational frequencies are intact, indicating the non-involvement of  $\text{N-NH-C=O}$  group in coordination.

The strong band at 1 645  $\text{cm}^{-1}$  in the spectrum of  $\text{AaInH}_2$  may be attributed to the aroyl carbonyl stretching mode<sup>11</sup>. In the spectrum of the  $\text{Ni}^{\text{II}}$  complex this band is found at the same frequency, indicating the non-participation of this carbonyl group in coordination, whilst in the spectra of the other metal chelates this band vanishes and a new band appears around 1 010–1 025  $\text{cm}^{-1}$ . This may be due to the  $\nu_{\text{C-O}}$  formed as a result of enolisation of aroyl  $\text{C=O}$  and subsequent coordination through the deprotonated oxygen. The amide-I band due to the anilide carbonyl stretching vibration in the spectra of both the ligands are observed in the region<sup>12</sup> 1 660–1 670  $\text{cm}^{-1}$ . In the spectra of all the metal complexes this band disappears while a new band appears around 995–1 025  $\text{cm}^{-1}$ . This may be attributed to the enolisation of the carbonyl group and subsequent coordination through the deprotonated oxygen atom. The new band may be assigned to  $\nu_{\text{C-O}}$  mode<sup>13</sup>. The azomethine stretching mode in the spectra of the ligands is observed at 1 570–1 580  $\text{cm}^{-1}$ . In the spectra of the complexes this band suffers a shift to lower frequency region, indicating the participation of azomethine nitrogen in coordination. Broad humps at 3 520  $\text{cm}^{-1}$  together with bands at 1 030–1 035  $\text{cm}^{-1}$  in the spectra of certain complexes are attributed to the coordinated water molecules.

The proton nmr spectrum of  $\text{AaINH}_2$  gives signals at  $\delta$  2.03 and 3.01 due to  $\text{CH}_3$  and  $\text{CH}_2$  protons respectively. The phenyl proton signals are observed at  $\delta$  7.00–7.52 as multiplets (**1b**). The pyridine ring proton signals are found at  $\delta$  7.58–9.00 as multiplets. The signals due to aromatic and hydrazide NH groups occur at  $\delta$  12.45 and 9.52 respectively. In the spectrum of  $[\text{Zn}(\text{AaIN})(\text{H}_2\text{O})_2]_n$ , the hydrazide NH proton signal disappears and the signal due to aromatic NH proton shifts to  $\delta$  11.00. The disappearance of the hydrazide NH proton signal may be due to the coordination of the oxygen atom of the system,  $\text{NH}-\text{C}=\text{O}$ , after enolisation and deprotonation. The  $\text{CH}_2$  signal is not observed in the spectrum of the complex. On the other hand, a new signal is observed at  $\delta$  4.51 which may be due to  $\text{CH}=\text{C}-\text{OH}$ . The phenyl and pyridine proton signals are observed at the same positions as in the ligand spectrum.

Thermal decomposition studies of  $\text{AaINH}_2$  complexes have been carried out so as to corroborate the informations obtained from the ir spectral studies about the status of water molecules present in some of these complexes as well as to know their general decomposition patterns. In the case of  $[\text{Co}(\text{AaIN})(\text{H}_2\text{O})_2]_n$  and  $[\text{Zn}(\text{AaIN})(\text{H}_2\text{O})_2]_n$ , the elimination of two water molecules take place between 130–200°. The second stage of degradation is slow and proceeds upto 600°, leading to the formation of respective oxides,  $\text{Co}_3\text{O}_4$  and  $\text{ZnO}$ . For  $[\text{Ni}(\text{AaINH})_2]$  the loss of one ligand molecule occurs at 210–400° and the second stage of decomposition (between 400 and 800°) leads to the formation of the oxide,  $\text{NiO}$ . Half of the ligand molecule from  $[\text{Cu}(\text{AaIN})]_n$  is lost at 200–370°, while it degrades to  $\text{CuO}$  at 370–580°.

Thus various spectral and physicochemical studies on the ligands and their complexes reveal that  $\text{AaH}$  behaves as a monovalent bidentate ligand coordinating through anilide carbonyl oxygen and azomethine nitrogen atoms, whereas  $\text{AaINH}_2$  behaves as a bivalent tridentate one coordinating through anilide carbonyl oxygen, azomethine nitrogen and aroyl carbonyl oxygen atoms, except for the  $\text{Ni}^{\text{II}}$  chelate, where it coordinates through anilide carbonyl oxygen and azomethine nitrogen

atoms alone. A polymeric structure may be assigned to the  $\text{Co}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  complexes of  $\text{AaINH}_2$  in order to match with their physicochemical properties and coordination requirements.

### Experimental

Acetoacetanilide, hydrazine hydrate, isoniazid and metal acetates used were of AnalaR grade. The solvents used were of reagent grade.

Acetoacetanilide hydrazone was prepared by adding hydrazine hydrate (1.0 g, 0.02 mol) in drops with vigorous stirring to acetoacetanilide (3.5 g, 0.02 mol) in minimum ethanol (15 ml). The colourless crystalline product was formed. Acetoacetanilide isonicotinoyl hydrazone was prepared as follows.

To a refluxing solution of isoniazid (1.7 g, 0.02 mol) in methanol (20 ml), ethanolic solution (20 ml) of acetoacetanilide (3.5 g, 0.02 mol) and a few drops of dilute  $\text{HCl}$  were added. The mixture was maintained at the refluxing temperature for 2 h. Slow evaporation gave crystalline product. The products were filtered, washed with water followed by ethanol and dried over  $\text{P}_4\text{O}_{10}$  under reduced pressure. The complexes were prepared by direct interaction of methanolic solutions of the ligands and the metal acetates. To a refluxing solution of  $\text{AaH}$  or  $\text{AaINH}_2$  (0.005 mol) in methanol (15 ml), was added in drops solution of the metal acetate (0.005 mol) in methanol (15 ml). The reaction mixtures were refluxed on a water-bath for 2–3 h. The resulting complexes were washed with methanol and dried under reduced pressure over  $\text{P}_4\text{O}_{10}$ .

The complexes were analysed by standard methods<sup>14</sup> to determine the percentage of metals present. The carbon, hydrogen and nitrogen analyses were carried out using a Heraeus CHN-O rapid analyser. The magnetic susceptibility was measured at room temperature using a Gouy magnetic balance with  $\text{Hg}[\text{CO}(\text{NCS})_4]$  as the reference compound. The magnetic susceptibility values were corrected for diamagnetism using Pascal's constants<sup>15</sup> and magnetic moments calculated. Electronic spectra were recorded on a Hitachi 3200 spectrophotometer in solid state, esr

spectra on a Varian E-109 spectrophotometer, proton nmr spectra ( $\text{CDCl}_3$ ) on a Bruker ACF (200 MHz) spectrometer and infrared spectra (KBr) with polystyrene as calibrant on a Perkin-Elmer 580 spectrophotometer. thermogravimetric measurement was performed on a Perkin-Elmer TGS-2 instrument with a heating rate of  $10^\circ/\text{min}$  in static air.

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