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N-Acetyl, N'-Benzoyl Hydrazine Complexes of Cobalt(II), Nickel(II) and Copper(II)

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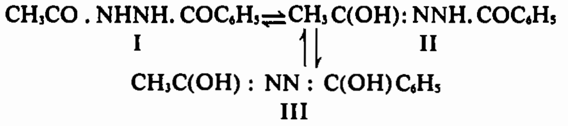
N-Acetyl, N'-benzoyl hydrazine (ABH) complexes of the type $M(ABH\text{-}H)_2 . 2H_2O$, M = Co^{II} and Ni^{II} and Cu(ABH-2H) have been prepared and characterised by analysis, visible and infrared spectral data and magnetic measurements. The complexes are spin free. ABH appears to be tridentate in octahedral Co^{II} and Ni^{II} complexes and quadridentate in square planar Cu^{II} complex. Chelation occurs through enolization of one or both the carbonyl groups.

Introduction

Hydrazine is known to lose its basic properties when one of the hydrogen atoms on each nitrogen atom is replaced by acyl groups.[1] N,N-diacetyl hydrazine has been shown to act as a quadridentate ligand forming chelates through enolization of both the carbonyl groups in some transition metal complexes.[2] The two carbonyl groups may behave differently when nucleophillic and electrophillic substituents are adjacent to them. For this reason, an unsymmetrical diacyl hydrazine viz., N′-acetyl, N,-benzoyl hydrazine (ABH) may react with metal ions in keto-enol form I, II or III.



$$\underset{\text{I}}{CH_3CO.NHNH.COC_6H_5} \rightleftharpoons \underset{\text{II}}{CH_3C(OH):NNH.COC_6H_5}$$
$$\updownarrow$$
$$\underset{\text{III}}{CH_3C(OH):NN:C(OH)C_6H_5}$$

It is with a view to investigate the behaviour of ABH towards metal ions that Co^{II}, Ni^{II} and Cu^{II} complexes have been prepared and their structural investigations reported in the present communication.

Experimental Section

Metal salts of B.D.H.,L.R. grade were used and ABH was prepared as described by Curtius.[3] Metals and hydrazine content in complexes were estimated following literature procedures.[4]

Visible and i.r. spectra were recorded on Cary 14 and Perkin Elmer 621 models respectively. Magnetic measurements were made on Faraday balance using $HgCo(CNS)_4$ as calibrant.

Complexes were prepared by mixing aqueous solutions of metal salts and dilute ethanolic solutions of ABH in 1:4 molar ratio and raising the pH either by sodium acetate in case of Cu^{II} complex or by ammonium hydroxide in case of Co^{II} and Ni^{II} complexes. The precipitates were filtered, washed with dilute ethanol and dried in desiccator. The analytical results and magnetic moments are given in Table(I).

Table I. Analytical data* and general characteristics of N-acetyl, N'-benzoyl hydraine complexes of Co^{II}, Ni^{II} and Cu^{II}.

Compound	Colour	Metal %	N_2H_4%	μ_{eff} B.M.
$Co(ABH\text{-}H)_2$	Light red	14.1 (14.0)	15.2 (15.2)	5.10
$Co(ABH\text{-}H)_2 . 2H_2O$	Light red	13.1 (13.1)	14.2 (14.3)	5.17
$Ni(ABH\text{-}H)_2$	Light green	13.9 (14.0)	15.1 (15.2)	3.30
$Ni(ABH\text{-}H)_2 . 2H_2O$	Dirty green	13.0 (13.1)	14.2 (14.2)	3.37
Cu(ABH-2H)		26.3 (26.5)	13.3 (13.3)	1.90

* Figures in parentheses are calculated values.

Results and Discussion

All the complexes are insoluble in water or non polar organic solvents and even in polar organic solvents like chloroform, dichloromethane and nitrobenzene. Freshly prepared Co^{II} and Ni^{II} complexes dissolve in pyridine giving orange-red and yellowish-green solutions respectively but the Cu^{II} complex remains insoluble. All the complexes decompose above 240°C without melting. The loss in weight of Co^{II} and Ni^{II} complexes at $\sim$ 110°C corresponds to two water molecules. Further there is no change in colour of the complexes. These observations indicate the presence of water molecules in lattice structure of the complexes.[5]

The high decomposition temperature may be related to their ionic or polymeric nature and the solubility of Co^{II} and Ni^{II} complexes in pyridine may be due to breaking up of such structures into simple monomeric complexes of the base. Fackler[6] and Richardson[7] have reported similar behaviour of

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metal acetyl acetonates which are polymeric clusters.[8] The 1 : 1 metal : ligand composition of Cu^{II} complex and its insolubility in pyridine indicate that it has a different polymeric structure from those of Co^{II} and Ni^{II} complexes.

Visible spectra of both aquated and anhydrous Co^{II} and Ni^{II} complexes in nujol show bands at 375, 475, 550, and 355, 610, 875 mμ respectively. In pyridine solutions the coresponding bands appear at 394, 550 mμ for Co^{II} complex and at 410, 625, 908 mμ for Ni^{II} complex indicating coordination of pyridine to central metal ions. These bands are in agreement to those observed for octahedral Co^{II} and Ni^{II} complexes.[9] Cu(AB), however shows a flat band centred at ~ 400 mμ. The tetrahedral Cu^{II} complexes absorb in near IR region.[10] Since Cu(AB) does not absorb in the range 1700-1800 mμ, the above mentioned flat band may contain more than one transition under the envelope. Such overlapping of bands arising out of some distortions in the square structure has been observed in case of some olive green square planar Cu^{II} chelates[11] with which Cu(AB) bears a colour similarity as well.

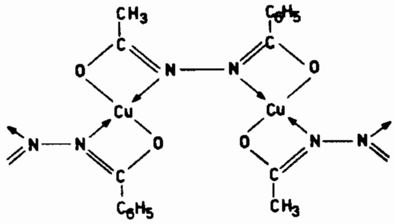
Magnetic measurements show that all the complexes are spin free. In Co^{II} and Ni^{II} complexes, the effective magnetic moments correspond to those observed for octahedral complexes.[12] Since one ABH molecule has four available donor atoms, it cannot be expected to occupy six octahedral sites. The Cu^{II} complex may therefore have four coordinate square geometry. The magnetic moment of Cu^{II} complex (1.9 BM) is fairly close to the values observed for square planar Cu^{II} complexes.[11] Cu(AB) may be an open chain polymer with N-N bridging unlike the dimeric (or polymeric) copper carboxylato complexes which show abnormally low magnetic moments.[13]

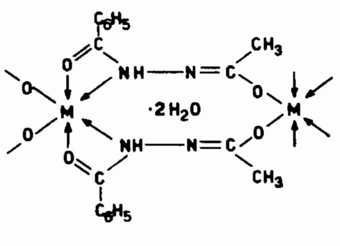
The i.r. spectra of ABH and its mono sodium salt SABH have been reported by Mashima.[14] The characteristic νNH at 3320 cm^{-1} and two amide I bands (νC=O) at 1720 and 1683 cm^{-1} in solution spectra of ABH are absent in Cu^{II} complex showing the loss of protons through enolization of the two carbonyl groups. The ν′ band of NCO^- group observed at 1528 cm^{-1} in the spectrum of SABH[14] shifts to 1517 cm^{-1} indicating involvement of tertiary nitrogen. The spectra of aquated Co^{II} and Ni^{II} complexes are markedly different from that of Cu^{II} complex and are very similar to the spectrum of SABH. Significant negative shifs of νNH and amide I bands from 3300 and 1637 cm^{-1} in SABH to 3180 and 1620 cm^{-1} respectively in Co^{II} and Ni^{II} complexes show bonding of — CONH — group to metals through oxygen of $>C=O$ and nitrogen of — NH — groups. The NCO^- group frequency observed at 1526 cm^{-1} indicates bonding through its oxygen atom.

The region below 1200 cm^{-1} is not well defined for hydrazine derivatives but N-N stretching frequency occurring in the range 1050-800 cm^{-1} has been identified and its shift has been found useful in understanding the involvement of nitrogen aftoms in coordination. νN-N has been shown to increase from 885 cm^{-1} in N_2H_4[15] to 973 cm^{-1} in $N_2H_5^+$[16] and 1024 cm^{-1} in $N_2H_6^{2+}$[17] due to protonation of one or both the nitrogen atoms. The protonation is akin to involvement of lone pairs of electrons on nitrogen atoms in coordination to metal ions. Onyszchuk[18] and Sacconi[19] have observed νN-N near the above quoted frequencies in the complexes containing unidentate and bidentate hydrazine respectively. But the above ranges in no way be taken as specific for coordination of one or two nitrogen atoms in substituted hydrazine complexes. In the i.r. spectrum of ABH several bands appear in the region below 1200 cm^{-1}. Eliminating the bands due to $-CH_3$ rocking and CH_3-C modes in the region 1050-900 cm^{-1} a band at 970 cm^{-1} may be assigned to νN-N. This band shifts to 1025, 995, and 980 cm^{-1} in Cu^{II}, Ni^{II}, and Co^{II} complexes respectively. When the magnitude of shift of νN-N is considered together with the composition and solubility of complexes in pyridine, it is logical to believe that both the nitrogen atoms are involved in coordination in Cu^{II} complex and one in Co^{II} and Ni^{II} complexes.

Water molecules are in lattice as the i.r. spectra of aquated and anhydrous Co^{II} and Ni^{II} complexes show very close similarity in the region below 1000 cm^{-1}. The expected peaks due to wagging, twisting and rocking modes of coordinated water at 900, 768, and 673 cm^{-1}[20] are not apparent.

Based on physico-chemical data, the following structures are proposed for the complexes:





M = Co^{II} and Ni^{II}

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