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NMR and IR Studies of Some Metal Complexes of 6-Substituted -1- Hydroxy-1,2,3-Benzotriazoles

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The ^1H NMR and IR spectra of 6-substituted-1-hydroxy-1,2,3-benzotriazoles have been measured. The IR spectra of the complexes of 6-substituted-1-hydroxy-1,2,3-benzotriazoles with different metal salts were also recorded in 4000–200 cm^{-1} region.

INTRODUCTION

Many workers have reported the spectral studies of triazoles and its derivatives and their metal complexes[1–7]. The present study deals with studies of NMR and IR spectra of 6-substituted-1-hydroxy-1,2,3-benzotriazoles and their metal complexes.

EXPERIMENTAL

^1H NMR studies were done on Perkin Elmer R-32 spectrometer and IR spectra was taken on Perkin Elmer-21 recording spectrometer. 6-Chloro-1-hydroxy-1,2,3-benzotriazole and 6-bromo-1-hydroxy-1,2,3-benzotriazole were prepared by method given by Joshi and Deorha[8] and 6-nitro-1-hydroxy-1,2,3-benzotriazole by Macbeth and Price[9]. These were recrystallised before use from hot water and dried in vacuum. The solutions of these reagents were made in ethyl alcohol. Metal salts solutions were prepared by dissolving AR grade metal salts (cobalt chloride, cadmium chloride and copper sulphate) in double distilled water.

RESULTS AND DISCUSSIONS

^1H NMR spectra of 6-substituted-1-hydroxy-1,2,3-benzotriazoles recorded in DMSO shows the clear pattern of splitting (Table 1). In 6-chloro-1-hydroxy-1,2,3-benzotriazole both *ortho* –CH coupling and *meta* –CH coupling are observed in the region δ – 7.42 to 8.30 ppm as singlet. The proton attached to –OH group is not observed. It may be present in water bond. The downfield shift of ring proton and merging of proton of –OH group in water bond indicates the exchange of protons between molecules.

^1H NMR spectra of 6-bromo-1-hydroxy-1,2,3-benzotriazole is quite similar to its chloro analogue. Splitting pattern is same. Here also both types of –CH coupling

TABLE 1

^{1}H NMR SHIFT OF 6-SUBSTITUTED-1-HYDROXY-1,2,3-BENZOTRIAZOLES

Triazoles	Proton Shift (δ ppm)			
6-Chloro-1-hydroxy-1,2,3-benzotriazole	8.30	8.14	7.73	7.41
6-Bromo-1-hydroxy-1,2,3-benzotriazole	8.38	8.26	7.92	7.57
6–Nitro-1-hydroxy-1,2,3-benzotriazole	8.68	8.30	7.96	7.59

are observed. The proton associated with ring system is observed as singlet in the region δ – 7.57 to 7.92 ppm. The proton of –OH group is measured in water bond. The ^{1}H NMR spectra of 6-nitro-1-hydroxy-1,2,3-benzotriazole is alike to its chloro and bromo analogues. Protons of the ring are observed in the region δ – 8.30 to 8.68 ppm.

IR spectra were recorded as KBr pellets. The spectra of 6-substituted-1-hydroxy-1,2,3-benzotriazoles show no absorption band in the region 1650–1700 cm^{-1} (Table 2), which can be assigned to ν(C=N) linkage. A band is present in the region 1590–1625 cm^{-1}, that can be assigned to ν(N=N) group. Werner *et al.*[10]

TABLE 2

N=N, N–OH, C–Cl, C–Br AND C–NO_2 IR FREQUENCIES (cm^{-1}) OF 6-SUBSTITUTED-1-HYDROXY-1,2,3-BENZOTRIAZOLES

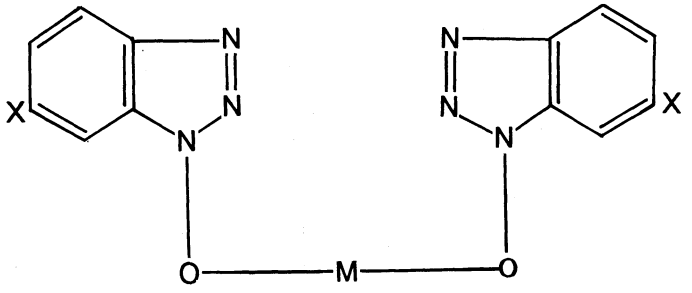
Triazoles	ν(N=N)	ν(N–OH)	ν(C–Cl)	ν(C–Br)	ν(C–NO_2)
6-Chloro-1-hydroxy-1,2,3-benzotriazole	1625	1210	670		
6-Bromo-1-hydroxy-1,2,3-benzotriazole	1625	1185		562.5	
6-Nitro-1-hydroxy-1,2,3-benzotriazole	1610	1210			1510

have shown the presence of ν(N=N) vibration near 1600 cm^{-1} in 1-acetyl-5-methoxy benzotriazole. IR spectra of 6-chloro-1-hydroxy-1,2,3-benzotriazole show band in the region of 650–670 cm^{-1}, 6-bromo-1-hydroxy-1,2,3-benzotriazole show absorption band at 560 to 575 cm^{-1} while a strong band appears in the region 1510–1525 cm^{-1} in 6-nitro-1-hydroxy-1,2,3-benzotriazole. The vibrations due to hydroxy group appear at 1185–1210 cm^{-1} region. Nakamoto[11] has shown ν(N–OH) absorption at 1192 cm^{-1}. The characteristic vibration frequencies of the ring system in 6-substituted-1-hydroxy-1,2,3-benzotriazoles have been observed in the region 1510–875 cm^{-1} (Table 3).

IR Spectra of Cu(II), Cd(II) and Co(II) Complexes of 6-Substituted-1-Hydroxy-1,2,3-Benzotriazoles

IR spectra of complexes of bivalent metals (Cu(II), Cd(II) and Co(II)) witn 6-substituted-1-hydroxy-1,2-3-benzotriazoles show absence of absorption band in 3200–3400 cm^{-1} which indicate absence of –NH group. No absorption band

is observed in the region 1630–1680 cm^{-1} indicating absence of ν(C=N) group. Absorption band in the region 1590–1620 cm^{-1} due to ν(N=N) group is fairly sharp. There is no sharp band in the region of 1190–1210 cm^{-1} which indicates the absence of –OH group. The absence of –OH frequency in spectra of the complexes indicate the complexation of metal through –OH group. The structure suggested of the complexes formed with bivalent metals is as follows:



X = –Cl,–Br or $-NO_2$; M = Co(II), Cu(II) or Cd(II)

TABLE 3
VIBRATIONAL FREQUENCIES OF THE RING SYSTEM IN 6-SUBSTITUTED-1-HYDROXY-1,2,3-BENZOTRIAZOLES

Triazoles	Vibrational Frequencies (cm^{-1})						
6-Chloro-1-hydroxy-1,2,3-benzotriazole	1510	1430 1375	1290	1240	1125	1080	910
6-Bromo-1-hydroxy-1,2,3-benzotriazole	1490	1375	1318 1300	1250	1125	1075	875
6-Nitro-1-hydroxy-1,2,3-benzotriazole	1490	1430 1400	1300	1240	1130	1050	850

TABLE 4
IR BANDS (cm^{-1}) OF COMPLEXES OF 6-CHLORO-1-HYDROXY-1,2,3-BENZOTRIAZOLES

S. No.	Complex	ν(N=N)	ν(C–Cl)
1.	Cu-6-chloro-1-hydroxy-1,2,3-benzotriazole	1590	610
2.	Cd-6-chloro-1-hydroxy-1,2,3-benzotriazole	1580	630
3.	Co-6-chloro-1-hydroxy-1,2,3-benzotriazole	1610	660

TABLE 5
IR BANDS (cm^{-1}) OF COMPLEXES OF 6-BROMO-1-HYDROXY-1,2,3-BENZOTRIAZOLE

S. No.	Complexes	ν(N=N)	ν(C–Br)
1.	Cu-6-bromo-1-hydroxy-1,2,3-benzotriazole	1620	562
2.	Cd-6-bromo-1-hydroxy-1,2,3-benzotriazole	1620	560
3.	Co-6-bromo-1-hydroxy-1,2,3-benzotriazole	1620	560

TABLE 6

IR BANDS (cm^{-1}) OF COMPLEXES OF 6-NITRO-1-HYDROXY-1,2,3-BENZOTRIAZOLE

S. No.	Complexes	ν(N=N)	ν(C–NO_2)
1.	Cu-6-nitro-1-hydroxy-1,2,3-benzotriazole	1600	1500
2.	Cd-6-nitro-1-hydroxy-1,2,3-benzotriazole	1600	1500
3.	Co-6–nitro-1-hydroxy-1,2,3-benzotriazole	1605	1510

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