Vibrational Spectral Studies of the Complexes of Diacetamide with Metal (II) Halides

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Summary: The FTIR Spectra between 4000-400 cm^{-1} and the Raman Spectra between 1800-1200 cm^{-1}, of the Complexes of diacetamide with metal (II) halides have been measured to distinguish the mode of coordination of ligand in these complexes. The diacetamide molecules in most of these complexes are acting as bidentate ligands, Coordinating through both of their carbonyl oxygen atoms and are in cis - form. In Co $[(DA)_4\ (H_2O)_2]\ Br_2$, although the diacetamide molecules are in cis - form but they are either acting as monodentate ligands or possibly two of them are uncoordinated as in the corresponding perchlorate complexes .

Introduction

Although, the solid diacetamide has been found to exist both in cis - (A) and in trans configurations (B) but the most stable form of the free ligand is dimeric (C) [1], in which both the molecules exist in trans -form (Fig. 1). The infra -red spectra of both the isomers of diacetamide and of their deuterated analogues have previously been carried out to assign the bands (1). Due to the difference in the configuration of the -CONHCO- group, remarkable difference have been observed between the infra - red spectra of the two isomers. Like biuret [2], in the spectrum of the trans form of diacetamide two well separated carbonyl stretching bands appeared at 1734 and 1700 cm^{-1} while in the infra- red spectrum of cis - form these bands were so close together that they appeared as a single band at 1734 cm^{-1} . Further, for the cis - isomer only a single band was observed in the imide (III) region whereas for trans - form two bands were seen clearly in this region. The Raman spectrum of diacetamide has been reported only in solution [3], and have not been recorded previously for any of its complexes reported here.

A number of complexes, formed by diacetamide with metal (II) halides and nitrates have been reported previously, and the ligand molecules have been suggested to exist in both cis - and trans - forms but physical studies were limited only to the infra - red, visible and electron spin resonance spectra [4-7], of few of them.

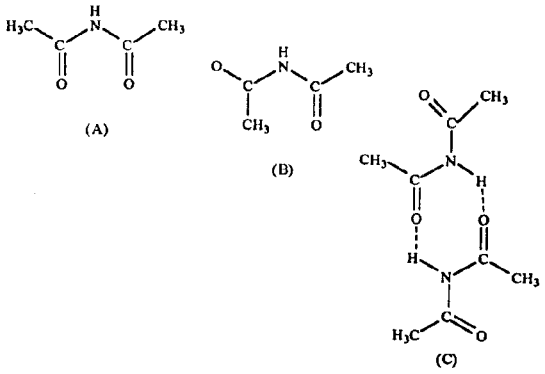

Fig. 1: Cis- (A), trans- (B) and dimeric- form (C) of Diacetamide.

Here, we report the FTIR and Raman spectra of the complexes, formed by diacetamide with a number of metal (II) halides, cobalt and nickel nitrates. They have been characterized by elemental analysis and the mode of coordination of diacetamide in all these complexes have been established by means of their FTIR and Raman spectra.

Results and Discussion

The characteristic bands in the FTIR (4000-400 cm^{-1}) and the Raman Spectra (1800 -1300 cm^{-1}) of the complexes of diacetamide with metal (II) halides, cobalt and nickel nitrates are listed in Table

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Table-1:Characteristic FTIR and Raman spectral bands of diacetamide complexes

Complex		C=0 Stretching Bands Imide I Band	Imide III Band
cis-Diacetamide (A)	IR	1734VS	1236S
trans-Diacetamide (C)	IR	1734 S 1700 S	1310 S 1223 S
	R	1745 S 1730 VS	1309 W 1223 W
$Co[(DA)_2 (H_2O)] Cl_2$	IR	1719 VS	1254 S
	R	1722 VS	
$Co[(DA)_2 (H_2O)_2] Br_2$	IR	1719 VS	1245 S
	R	1720 VS	1253 W
$Co(DA)_2Cl_2$	IR	1724 S	1254 S
	R	1718 VS	1253 W
$Co[(DA)_4 (H_2O)_2] Br_2$	IR	1725 S 1691 S	1252 S
	R	1731 S 1716 VS	1242 M
$Co(DA)_2 (NO_3)_2$	IR	1724 VS	1263 S
$Ni[(DA)_2 (H_2O)_2] Cl_2$	IR	1722 VS	1253 S
	R	1728 VS	
$Ni[(DA)_2 (H2O)_2] Br_2$	IR	1716 VS	1254 S
	R	1728 VS	1252 W
$Ni(DA)_2 (NO_3)_2$	IR	1724 VS	1259 S
$Mg[(DA)_2(H_2O)_2]Cl_2$	IR	1734 VS	1255 S
	R	1737 VS	
$Mg[(DA)_2 (H_20)_2]Br_2$	IR	1732 VS	1256 S
	R	1740VS	1250 W

VS= Very Strong, S= Strong M= Medium, W= Weak.

1, together with the infra-red frequencies reported for cis- and trans-forms of the free ligand [1].

The infra-red spectra of some of these complexes have previously been reported [4-5] and are in good agreement with the present results. The diacetamide molecules in most of these complexes are acting as bidentate ligands, coordinating through both of their carbonyl oxygen atoms and are in cis-form (A), since the spectra closely parallel that of uncomplexed cis-diacetamide. The criterion for the existance of bonding through oxygen in all these complexes is the shifting of the carbonyl stretching frequencies, imide I band, towards the lower frequency side and of C-N stretching frequencies towards the higher side.

In the FTIR spectra of all these diacetamide complexes except $Co[(DA)_4 (H_2O)_2] Br_2$, the frequency of carbonyl stretching vibration (at 1734 cm^{-1} in the ligand) decreases considerably, indicating that the diacetamide molecules have been coordinated with the metal ions through their carbonyl oxygens.

Further, in the FTIR spectra of these complexes, the C-N stretching band (imide III band) appear at higher frequencies compared with the free ligand. All these band shifts, on complex formation, are consistant with a decreased C=O bond order and an increased C-N bond order.

Only the infra-red spectrum of $Co[(DA)_4 (N_2O)_2] Br_2$ differs in one respect from the rest of the cis- form complexes. Instead of a single carbonyl absorption around 1720 cm^{-1}, there is a doublet at 1725 and 1691 cm^{-1}. This suggests that while the diacetamide molecules appear to be in the cis-form, the carbonyl groups are probably not all equivalent.

Raman spectra of trans-diacetamide and the complexes with metal(II) halides, cobalt and nickel nitrates were recorded in the region 1800- 1200 cm^{-1} (Fig.2). As the cis- form is extremely difficult to isolate and is unstable [6], all attempts to measure the Raman spectrum of diacetamide in this configuration were unsuccessful.

In the Raman spectrum of trans-diacetamide, as in the infra-red, two well separated bands appeared in the carbonyl stretching region and two weak bands could be seen in the imide III region (Fig. 2). In the Raman spectra of all the diacetamide complexes, studied in the present work, there is a single carbonyl stretching band and a single band in the imide III region, in agreement with the infra-red results and indicates the cis- coordination of ligand molecules. It seems that this is the characteristic of the cis-bidentate arrangement of the ligand. Like infra-red, in the Raman spectra of these complexes, the carbonyl stretching band (imide I band) appeared at lower frequencies than free ligand suggesting coordination through carbonyl oxygen atoms. These results are also in line with the Raman spectral studies of cis-biuret complexes [8].

In the Raman spectrum of $Co[(DA)_4 (H_2O)_2] Br_2$, a doublet appeared in the carbonyl region (Fig.2) and only a single band could be seen in the imide III region. This supports the previous suggestion that, although the diacetamide molecules in this complex are in cis- configuration (A), they are either acting as monodentate ligands, or possibly two of them are uncoordinated as in the corresponding perchlorate complexes [9].

Experimental

All of these complexes were prepared by the previously reported method [4-7]. Found:- C, 26.02; H, 4.86; N, 7.39 Calculated for Co $[(DA)_2 H_2O)_2] Cl_2$:- C, 26.09; H, 4.89; N,7.61. Found:- C, 20.80; H, 3.91; N,6.18 Calculated for $Co[(DA)_2 H_2O)_2] Br_2$, C, 21.01; H, 3.94; N, 6.13. Found- C, 28.24; H, 4.74; N, 8.38 Calculated for Co $(DA)_2 Cl_2$:- C, 28. 92; H, 4.22; N, 8.43. Found:- C, 29.19; H, 4.84; N, 8.59

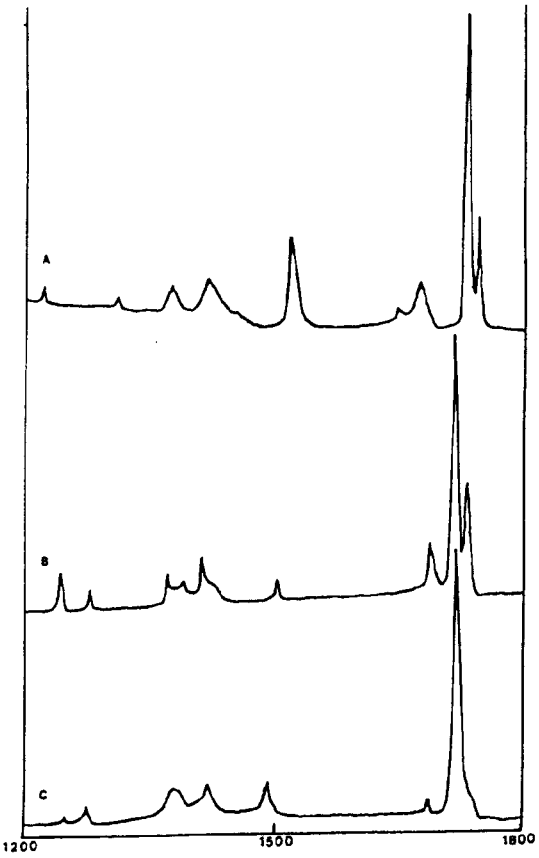

Fig.2: Raman Spectra of: A) Diacetamide (trans-): B) Co $[(DA)_4 (H_2O)_2] Br_2$; C) Co $[(DA)_2 (H_2O)_2] Br_2$;

Calculated for $Co[(DA)_2(NO_3)_2] Br_2$ C, 29. 14; H, 4.86; N, 8.50. Found:- C, 25.23; H, 3.55; N, 14.64 Calculated for Co $(DA)_2 (NO_3)_2$ C, 24, 93; H, 3.63; N, 14.54. Found C, 25.95; H. 4.85; N, 7.51 Calculated for Ni $[(DA)_2 (H_2O)_2] Cl_2$:- C, 26. 11; H, 4.89; N, 7.61. Found : - C. 20. 24; H, 3.63; N, 5.95 Calculated for Ni $[(DA)_2 H_2O)_2] Br_2$ - C. 21.02; H, 3.94; N, 6.13. Found:-C, 25.47; H, 3.88; N, 13.46 Calculated for Ni $(DA)_2 (NO_3)_2$:- C. 24.95; H, 3.64; N. 14.56. Found:- C, 28. 66; H, 5.30; N, 8.52 Calculated for $Mg[(DA)_2 H_2O)_2] Cl_2$:- C28.80; H, 5.40; N, 8.40. Found C. 22.41; H, 4.16; N. 6.60 Calculated for $Mg[(DA)_2 (H_2O)_2] Br_2$:- C, 22.73 H, 4.26; N, 6.63.

Elemental analysis for % composition of C, H and N were carried out by the Microanalytical Laboratory Imperial College of Science, Technology and Medicine, London.

FTIR spectra were obtained using a Perkin-Elmer 1720 FTIR spectrometer. Raman spectra were measured on a Spex Ramlog-V spectrometer and Spex Datamate computer control unit, using the exciting line at 568.2 nm from a Coherent Innova 90 Krypton-ion laser and 488.0 nm from a Coherent Innova 70 Argon-ion laser. Spectra were taken from solid samples by the method described previously [10].

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