Raman Spectral Studies of the Complexes of Biuret with Metal(II) Halides

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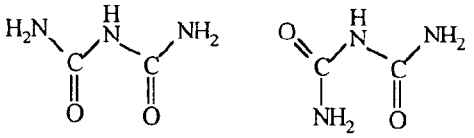
Summary: As the biuret can adopt either the cis- or the trans-configuration in its complexes, the Raman spectra have been measured for the complexes of biuret with metal(II) halides and the modes of coordination, of lignand in all these complexes, have been established. The complexes $N(biuret)_2X_2$ (M= Mn & Co; X= Cl or Br and M= Ni and Zn; X = Cl) have been found to contain biuret in the cis-configuration, coordinating with metal ions through both of its carbonyl oxygen atoms. On the other hand, complexes $M(biuret)_2Cl_2$ (M= Ca, Cd and Hg) and $Cd(biuret)_2Br_2$ contain biuret in the trans-configuration, coordinating through one of the two carbonyl oxygen atoms. These results are consistent with the previously reported I.R and E.S.R. spectral studies [1,2].

Introduction

The knowledge about the active sites, in complexed metallic biomolecules, can be achieved by using model complexes having similar ligands, with the presence of the same structural groups as larger biomolecules and employing various instrumental techniques. In this context, the rapid development of the field of bioinorganic chemistry has largely been due to the study of simple models by applying various instrumental techniques as N.M.R., E.S.R., I.R. and Raman spectroscopy, in addition to improved methods of X-ray diffraction. The present work includes the structural study of the complexes of biologically important divalent metals with oxygen-donor ligand, biuret. Such complexes are of importance in modeling the interaction of metal ions with peptides and proteins.

Although, in solid biuret exists in trans-arrangement, with intra-molecular hydrogen-bond [3], when it acts as a ligand it can adopt either the cis- (1A) or the trans- (1B) configuration (Fig. 1).



(IA) (IB)

Fig. 1: Cis- (IA) and trans- configuration (IB) of biuret.

In the X-ray crystal structure of $Zn(biuret)_2Cl_2$ [4], biuret is bound to the metal as a bidentate ligand via two oxygen atoms and is in cis- configuration (1A). The same type of structure has been inferred, from spectral data, for Mn, Co and Ni complexes [2,5].

On the other hand, in the corresponding Ca, Cd and Hg complexes, biuret adopts the monodentate trans- configuration (1B) with an intra-molecular hydrogen bond [1,2,6,7].

Here, we report the Raman spectral studies of the complexes of biuret with metal(II) halides. The mode of coordination of biuret in all these complexes have been established by means of the Raman spectra.

Results and Discussion

The characteristic bands in the Raman spectra (1800 - 1300 cm^{-1}) of biuret and its complexes studied in the present work are listed in Tables 1 and 2.

The biuret molecules can adopt either the cis- or the trans- configuration in its complexes and considerable differences can be expected between the Raman spectra of both types. Although, the infra red spectra for both types of complexes have been reported and normal coordinate analysis have

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Table-1: Characteristic Raman spectral bands of cis- biuret complexes.

Complex	C=O Stretching bands		Imide II band	Imide III band
$Mn(biuret)_2Cl_2$	1681 VS	1678 sh	1481 S	1352 W
$Mn(biuret)_2Br_2$	1683 VS	1675 S	1483 S	1354 W
$Co(biuret)_2Cl_2$	1682 S	1675 VS	1486 S	1356 W
$Co(biuret)_2Br_2$	1685 S	1673 VS	1490 S	1357 W
$Ni(biuret)_2Cl_2$	1679 VS	1675 VS	1485 S	1356 W
$Zn(biuret)_2Cl_2$	1680 VS	1675 S	1481 S	1355 W

VS = Very Strong, S= Strong, W= Weak, Sh= Shoulder.

Table-2: Characteristic Raman spectral bands of trans - biuret complexes.

Complex	C=O stretching band	Imide II band	C-N Stretch band
Biuret	1690 VS	1511 S	1423 W
$Cd(biuret)_2Cl_2$	1672 VS	1582 S	1448 S
$Cd(biuret)_2Br_2$	1669 VS	1580 S	1438 M
$Hg(biuret)_2Cl_2$	1667 VS	1581 M	1436 M
$Ca(biuret)_2Cl_2$	1675 S	1581 S	1445 Br

been carried out to assign the bands [1,8,9], Raman spectra have not been reported previously for any of them.

The complexes, $M(biuret)_2X_2$ (M= Mn and Co) X= Cl or Br and M= Ni and Zn; X= Cl) seem to contain biuret in the cis configuration (1A), coordinating with metal ions through both of its carbonyl oxygen atoms (Table-1). This can readily be seen from the Raman spectra where both of the carbonyl stretching bands are very well resolved and can be seen clearly (Fig. 2). This result is in line with the I.R. and E.S.R. spectral results reported previously [1,2,5].

On the other hand, the complexes $M(biuret)_2Cl_2$ (M= Ca, Cd and Hg) and $Cd(biuret)_2Br_2$ contain monodentate biuret which appears to be in the trans- configuration (1B), coordinating through one of the two carbonyl oxygen atoms. The Raman spectra of these trans-biuret complexes are very different from those with biuret in cis- configuration. In contrast to their infra-red spectra [1], only one of the two carbonyl stretching bands is observed in the Raman spectra of these complexes, similar to that of uncomplexed biuret (Table-2). The similarity of the Raman spectra of these complexes with that of uncomplexed biuret also confirms the presence of the trans-configuration of ligand, coordinating through one of the two carbonyl oxygens. In these

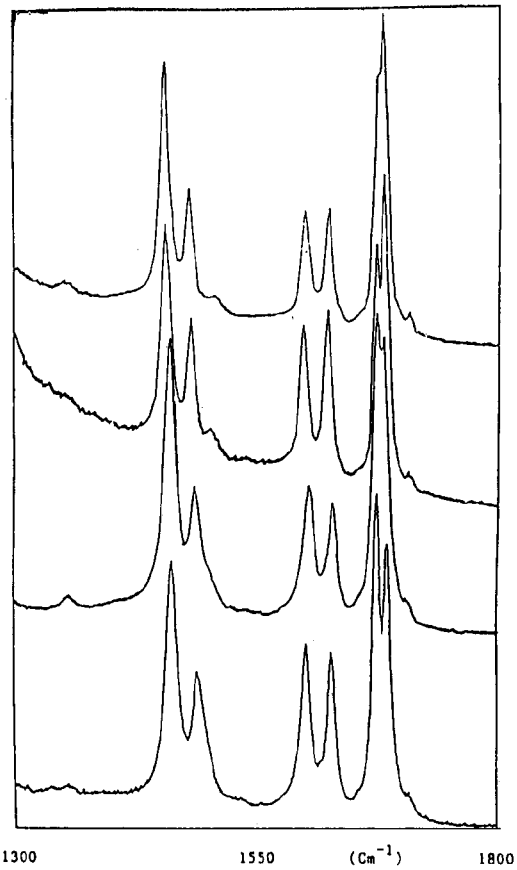

Fig. 2: Raman spectra of : A) $Mn(biuret)_2Cl_2$; B) $Mn(biuret)_2Br_2$ C) $Co(biuret)_2Cl_2$; D) $Co(biuret)_2Br_2$

complexes, carbonyl stretching band appeared at lower frequency than for solid biuret indicating the coordination of the ligand with metals through the carbonyl oxygen atom.

The criterion for the existence of bonding through oxygen in all these complexes is the shifting of the carbonyl stretching frequencies imide I_s(symmetric) and imide I_{as}(asymmetric) bands, towards the lower frequency side and the shifting of C=N stretching frequencies towards the higher frequency side. All of these complexes show a decrease in the frequencies of carbonyl stretching bands and an increase in the frequency of C-N stretching band. These shifts are consistent with a decreased C=O order and an increased C-N bond order and confirm that the coordination of biuret

with metal in all these complexes is through carbonyl oxygens. These results are also in line with the previously reported I.R. and E.S.R. spectral data [1,2].

Experimental

Preparation of complexes

All the chemicals used in the present work were pure analytical grade and were used without further purification.

$M(biuret)_2X_2$ (M= Mn, Co and Cd; X= Cl or Br: M= Ni and Hg: X= Cl)

These complexes were prepared by adding the hot solution of hydrated metal(II) halide (0.01 mole) in ethanol (80 cm^3) to a hot solution of biuret (2.06 g; 0.02 mole) in ethanol (160 cm^3). The resultant mixture was allowed to cool to room temperature and the precipitates thus formed was filtered off, washed with cooled ethanol and dried in vacuo over P_2O_5. Found: C, 14.59; H, 3.00; N, 24.98; Calculated for $Mn(biuret)_2Cl_2$: C, 14.46; H, 3.01; N, 25.30, Found: C, 11.78; H, 2.37; N, 19.92 Calculated for $Mn(biuret)_2Br_2$: C, 11.40; H, 2.38; N, 19.95. Found: C, 14.61; H, 2.96; N, 25.14 Calculated for $Co(biuret)_2Cl_2$: C, 14.29; H, 2.98; N, 25.00. Found: C, 11.70; H, 2.36; N, 20.00 Calculated for $Co(biuret)_2Br_2$: C, 11.29; H, 2.35, N, 19.76; Found: C, 12.82, H, 2.48, N, 21.14 Calculated for $Cd(biuret)_2Cl_2$: C, 12.33; H, 2.57; N, 21.57. Found: C, 10.40; H, 2.07; N, 17.40 Calculated for $Cd(biuret)_2Br_2$: C, 10.03; H, 2.09; N, 17.56. Found: C, 14.20; H, 2.89, N, 24.37. Calculated for $Ni(biuret)_2Cl_2$: C, 14.30; H, 2.98; N, 25.02. Found: C, 11.11, H, 2.08; N, 17.93 Calculated for $Hg(biuret)_2Cl_2$: C, 11.05; H, 2.09; N, 17.59.

$Zn(biuret)_2Cl_2$

This complex was prepared by the previously reported method [2]. Found: C, 15.09; H, 2.84; N, 25.09 Calculated for $Zn(biuret)_2Cl_2$: C, 14.02; H, 2.92; N, 24.53.

$Ca(biuret)_2Cl_2$

A warm solution of calcium chloride (0.555g, 0.005 mole) in ethanol (20 cm^3) was added to a warm solution of biuret (2.06g, 0.02 mole) in ethanol (120 cm^3). The reaction mixture was refluxed for three hours and the white precipitate of $Ca(biuret)_2Cl_2$ thus formed was filtered off, washed with ethanol and dried in vacuo over P_2O_5. Found: C, 15.41; H, 3.16; N, 26.28 Calculated for $Ca(biuret)_2Cl_2$: C, 15.41; H, 3.15; N, 26.50.

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

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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