

Preparation and ESR Study of the Complexes of L-histidine with Zinc and Cadmium

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Summary: The preparation of the complexes Zn(Mn) (L-His)₂ and Cd(Mn) (L-His)₂ are reported. The E.S.R. spectra, at both X- and Q-band of Mn(II) ions doped in these complexes and also those of M(L-His)₂·2H₂O (M = Zn and Cd) are reported, and the zero-field splitting parameters D and λ ($\lambda = E/D$) are deduced. Considerably higher values of D and λ observed for M(Mn) (L-His)₂·2H₂O (M = Zn and Cd) suggest quite appreciable deviation from regular symmetry, as would be expected from their crystal structure studies [1-2]. The distinctly lower values of D and λ observed for anhydrous complexes, M(Mn)(L-His)₂ (M = Zn and Cd), suggest geometries tending, most probably, towards regular octahedral structures. The negative sign of D observed from the Q-band spectra of these complexes, suggests that the principal D-tensor axis lies along the line of two Cd-N bonds, and the coordinated oxygens from the carbonyl groups are in cis-positions.

Introduction

Of all the possible model studies of metal ions with biologically important ligands, those relating to metal-amino acid interactions have been the longest studied [3]. As the proteins contain the same type of donor groups, therefore, the complexes of amino acids act as models for the metal binding sites on proteins.

Histidine is an optically active α -amino acid that occurs in its leavo form in many proteins. It has

four possible sites at which a metal could become complexed. It is important biochemically since it is likely by virtue of its basic chelating characteristics that the histidyl group is present at the active or allosteric sites of certain enzymes. In the complexes studied here, histidine is behaving as an anion (A).

Here, we report the preparations of complexes M(L-His)₂ (M = Zn and Cd). The E.S.R. spectra of Mn(II) ions doped into the lattices of

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these complexes and also of $M(L\text{-His})_2 \cdot 2H_2O$ ($M = Zn$ and Cd) have been obtained to study their structures. Complexes of zinc and cadmium, with the general formula $M(L\text{-His})_2 \cdot 2H_2O$ have previously been prepared and their crystal structures have been determined [1-2]. In both of these complexes, metal ions are primarily coordinated tetrahedrally to four nitrogens and very loosely associated with two oxygens, and the frame work of hydrogen bonds holding the molecules together is the same. The shape of the co-ordination group around metal ions is very far from a regular octahedron.

Results and Discussion

E.S.R. spectra have been obtained at both X- and Q-band frequencies for 1% of $Mn(II)$ ions doped in to the compounds $M(L\text{-His})_2 \cdot 2H_2O$ ($M = Zn$ and Cd) and $M(L\text{-His})_2$ ($M = Zn$ and Cd).

At X-band, all the complexes gave good quality but very complicated spectra (Fig. 1) with considerable overlapping of transitions and detailed interpretation was very difficult. The highest band observed around 715 mT, in the spectra of complexes $M(L\text{-His})_2 \cdot 2H_2O$ ($M = Zn$ and Cd), suggested D values of about 0.09 cm^{-1} .

The Q-band spectra of all of these complexes were very well resolved, and therefore, were used to determine the precise values of zero-field splitting

parameters, D and λ ($= E/D$), in the Spin Hamiltonian (i)

$$= g \beta BS + D(S_z^2 - 1/3S(S+1)) + E(S_x^2 - S_y^2) \quad (i)$$

The observed resonance fields fitted very well with those calculated, using the programme ESR5 [5], by exact diagonalization of the matrix derived from (i) with $g_{iso} = 2.00$ (Tables 1-2).

Like diacetamide complexes [6], at Q-band frequency, a difference was observed between the mean hyperfine spacing of the sextets for the extreme Z-axis transitions, for the complexes of L-histidine. For all these complexes, the spacing was greater on the lowest field than on the highest field transition, so D is negative.

Values of D and λ are listed in Table 3. The values of D and λ , for complexes $M(L\text{-His})_2 \cdot 2H_2O$ ($M = Zn$ and Cd), are closely similar to one another but entirely different from those of the anhydrous analogues. These values suggest quite considerable deviation from regular symmetry, as would be expected from the crystal structures of these hydrated complexes [1-2].

The negative sign of D found for these hydrated complexes suggest that the principal D tensor axis lies along the two metal-nitrogen bonds. This is consistent with the crystal structure studies of these complexes [1-2]. The sizeable rhombic dis-

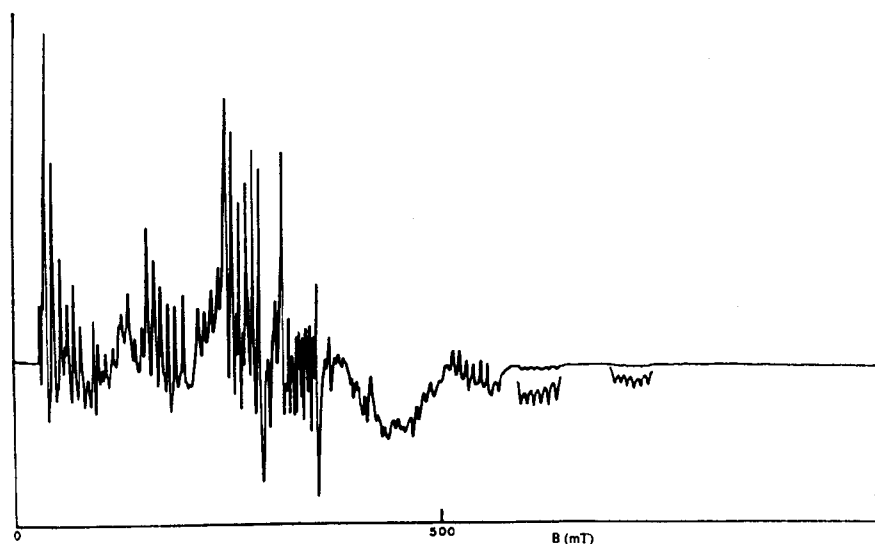


Fig.1: X-band ESR spectrum of $Cd(Mn)(L\text{-His})_2 \cdot 2H_2O$.

Table 1: Q-band ESR spectrum (mT) of Zn(Mn) (L-His)₂·2H₂O

Observed ($\nu = 33.760$ B. GHz)	Calculated for $D = -0.092 \text{ cm}^{-1}, \lambda = 0.179$		Field direction	Levels
B.	T.P.			
442.8 W				
548.8 W				
815.3 W	815.6	5.38	Z	6-5
912.9 W	912.3	4.33	Y	2-1
1011.6 M	1009.3	8.30	Z	5-4
1052.5 M/S	1051.0	7.35	Y	3-2
1128.2 W/M	1127.2	4.10	X	2-1
1147.6 M/S	1147.9	7.18	X	3-2
1184.5 S	1183.8	8.85	X	4-3
1196.4 S	1195.6	8.81	Y	4-3
1204.9 S	1204.0	9.08	Z	4-3
Region:	1236.2	8.67	X	5-4
1308.6 M	1306.5	6.00	X	6-5
1348.9 M/S	1348.2	8.39	Y	5-4
1400.1 M	1400.3	7.83	Z	3-2
1511.8 W	1511.0	5.65	Y	6-5
1600.5 W	1598.6	4.74	Z	2-1

Table 2: Q-band ESR spectrum (mT) of Cd(Mn) (L-His)₂

Observed ($\nu = 33.810$ B. GHz)	Calculated for $D = -0.074 \text{ cm}^{-1}, \lambda = 0.050$		Field Direction	Levels
B.	T.P.			
891.3 W	893.0	5.07	Z	6-5
1031.9 W	1032.4	4.39	Y	2-1
1049.9 M	1050.3	8.06	Z	5-4
	1080.5	4.34	X	2-1
1110.5 M	1112.6	7.44	Y	3-2
1133.6 M	1134.7	7.39	X	3-2
1196.1 S	1196.5	8.89	X	4-3
1198.5 S	1198.6	8.88	Y	4-3
Region:	1207.7	9.01	Z	4-3
1267.5 M	1266.7	8.47	X	5-4
1291.8 M	1291.6	8.41	Y	5-4
	1346.4	5.70	X	6-5
1363.8 M/W	1365.1	7.96	Z	3-2
1394.0 W	1392.6	5.62	Y	6-5
1521.6 W	1522.7	4.94	Z	2-1

tortion shown by the higher values found for these complexes are probably due to deviations from the 90° angle.

The similarity of structures between M(L-His)₂ (M = Zn and Cd) is quite clear from their identical values of D and λ . These values are distinctly lower than for the hydrated analogues, suggesting geometries tending, most probably, towards regular octahedral structures. Again, the negative sign of D suggests that in these complexes, like their hydrated analogues, the principal D-tensor axis lies

Table 3: Zfs parameters of Mn(II) in L-Histidine complexes

Complex	D (cm ⁻¹)	λ
Zn (L-His) ₂ ·2H ₂ O	-0.092	0.179
Cd(L-His) ₂ ·2H ₂ O	-0.091	0.126
Zn (L-His) ₂	-0.071	0.090
Cd (L-His) ₂	-0.074	0.050

along the line of two Cd-N bonds, and that coordinated oxygens from the carboxyl groups are in cis-positions.

From these results it appears that in complexes M(L-His)₂·2H₂O (M = Zn and Cd), the hydrogen bonding, between the carboxyl oxygens and the water hydrogens, is playing an important role in maintaining their structures. On dehydration, due to the absence of hydrogen bonding, the carboxyl groups of L-histidine molecules become free to move and most probably come closer to the central metal ions. This would result in more regular octahedral structures and the lower values of D and λ as observed for the anhydrous complexes, M(L-His)₂ (M = Zn and Cd).

Experimental

Preparation of complexes

All reagents used were of A.R. grade and were used without further purification.

M(Mn) (L-His)₂·2H₂O (M = Zn or Cd)

Metal carbonate (0.01 mole) and manganese (II) carbonate (0.0001 mole) were dissolved in hot water (20 cm³). It was then mixed with a warm solution of L-Histidine (0.04 mole) in water (20 cm³) and the mixture was heated for 1 hour. The resulting solution was filtered off and allowed to evaporate at room temperature for several days. The fine crystals thus formed were dried in vacuo at room temperature. Found: - C, 34.51; H, 4.78; N, 20.09. Calculated for Zn(L-His)₂·2H₂O: - C, 35.17; H, 4.88; N, 20.52. Found: - C, 31.79; H, 4.28; N, 18.58. Calculated for Cd(L-His)₂·2H₂O: C, 31.55; H, 4.38; N, 18.40.

M(L-His)₂ (M = Zn or Cd)

These complexes were prepared by drying the corresponding hydrated complexes *in vacuo* at 100°C for 16 hours. Found:- C, 38.17; H, 4.22; N, 22.33. Calculated for Zn(L-His)₂:- C, 38.56; H, 4.28; N, 22.50. Found:- C, 33.68; H, 4.66; N, 19.47. Calculated for Cd(L-His)₂:- C, 34.25; H, 3.81; N, 19.98.

Analytical results were obtained by the Imperial College Microanalytical Laboratory.

For the E.S.R. study the normal doping level was 1% of manganese in all cases. E.S.R. spectra were obtained as described previously [4], using polycrystalline samples at room temperature.

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