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Note

SYNTHESIS OF SOME METAL CHELATES OF L-LYSINE MONOHYDROCHLORIDE

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Jain et al. [1] reported the studies on Fe(II) and Cd(II) chelates of L-lysine monohydrochloride. In the present communication, attempts are made to report the complexes of L-lysine monohydrochloride with Mg(II), Mn(II) and Hg(II) metal ions. Although complexation behaviour of L-lysine has been extensively studied [2–6], a perusal of the literature [7,8] has revealed that no work has been done on the bivalent metal chelates of L-lysine monohydrochloride. Some very interesting work has been reported on compounds acting as antidotes against manganese poisoning [9,10]. A very important use of L-lysine hydrochloride introduced by Hayushi et al. [11] and Hoffman [12] is in the conservation of blood. It has also been found [13] that L-lysine monohydrochloride increases the yield of cereals. The use of L-lysine monohydrochloride as a mouth wash has been proposed by Schmitt et al. [14].

EXPERIMENTAL

The chemicals and apparatus employed in the investigations are the same as those reported earlier (1). Thermogravimetric analyses were carried out using a modern thermogravimetric balance with a Toshaiwl furnace at a heating rate of 10° $\min^{-1}$. L-Lysine monohydrochloride and its chelates with Mg(II), Mn(II) and Hg(II) were isolated by the method reported earlier [1].

The results of elemental analysis, magnetic moment and conductance of the chelates are summarised in Table 1.

RESULTS AND DISCUSSION

The conductance measurements of the resulting solutions revealed that all the metals form complexes with ligand in the ligand:metal molar ratio of 2:1.

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TABLE 1

Elemental analysis results and magnetic moment and conductance data of the chelates

Sample	Complex	Carbon (%)		Hydrogen (%)		Nitrogen (%)		μ_{eff} (B.M.)	Conductance (ohm^{-1} cm^2)
		Found	Calcd.	Found	Calcd.	Found	Calcd.		
1	$C_{12}H_{26}N_4O_4Mg \cdot 6\,H_2O$	34.0	34.1	8.80	9.0	12.9	13.2	0.83	5.3
2	$C_{12}H_{26}N_4O_4Mn \cdot 4\,H_2O$	34.3	34.5	8.0	8.1	13.2	13.4	1.75	4.2
3	$C_{12}H_{26}N_4O_4Hg \cdot H_2O$	26.1	26.2	5.1	5.5	11.0	11.2	0.76	7.2

The chelates gave satisfactory elemental analyses and display 2:1 ligand:metal stoichiometry. The composition may be expressed by $L_2M \cdot nH_2O$, where M = metal ion.

The magnetic moments (Table 1) indicate the presence of one unpaired electron in Mn(II) chelate, showing the paramagnetic character. The remaining chelates, Mg(II) and Hg(II), were found to be diamagnetic because unpaired electrons were absent in both chelates. From the magnetic moments it is apparent that there is no metal–metal bonding in the chelates and hence spin exchange does not take place. The negligibly small conductance values (5.3–7.2) of the compounds in double distilled water suggest them to be non-electrolytes.

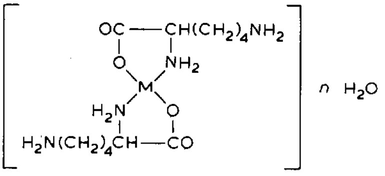
The thermogravimetric results of all the complexes are given below. The weight loss curve indicates that all complexes dehydrated at 60–140°C, suggesting that water is present in the complexes as lattice water. The major part of the reaction takes place between 150 and 400°C in all complexes. The end product of decomposition was obtained around 500–550°C by weight loss curve and chemical analysis. The plateau occurring above 500°C corresponds to metal oxides. The results were also supported by the differential thermal analysis curves. The percentage weight loss observed for different products formed during heating almost coincides with the calculated figure.

The following principal bands (cm^{-1}) were obtained in the IR spectra of the ligand and its chelates.

	$\nu(NH_3Cl)$	ν_{asym} (COO^-)	ν_{sym} (COO^-)
Ligand	2100	1560	1390
Mg chelate		1580	1380
Mn chelate		1620	1370
Hg chelate		1595	1395

The band at 2100 cm^{-1} in the ligand and assigned to the NH_3^+Cl group [15] disappears in chelates due to the fact that the chelates were isolated at pH about 8.0 and therefore the NH_3^+ group was deprotonated. It is well known that amino acids [16] exist as dipolar Zwitter ions in the crystalline state and therefore the two relevant IR bands of amino acids from the coordination point of view are the antisymmetric and symmetric stretching frequencies of the carboxyl group. Of these, the antisymmetric (COO^-) stretching frequency is much more sensitive [17] than the symmetric and its value in a complex is a function of the mass, radius, charge and electronegativity of the metal. Thus any shift in ν_{asym} (COO^-) in Mg(II) and Hg(II) chelates is significantly increased to a higher value, indicating coordination of the carboxyl group to the metal. The increase in frequency is due to formation of M–O [16–18], which lengthens one C–O bond, thereby making the two oxygen atoms non-equivalent. Thus by M–O bond formation, the asymmetry of the COO^- group is increased and thereby ν_{asym} (COO^-) is also increased. It is therefore, expected that the more covalent the character of the M–O bond, the more would be the shift of ν_{asym} to a higher frequency.

The IR spectrum of the ligand also has a broad band in the 2800–3400 cm^{-1} region, evidently due to O–H and N–H stretching, and it almost remains intact in the spectra of chelates. On the basis of the above IR evidence, the chelates may be assigned the structure [8]



where M = Mg, Mn or Hg and n = 6 for Mg(II), 4 for Mn(II) and 1 for Hg(II).

The X-ray powder photographs of all the complexes have been studied by Bragg's equation

$\lambda = 2d \sin\theta$

The grazing angle, θ, and the lattice spacing value, d, and relative intensity have been calculated by using a value of 1.5418 Å for λ. The study indicates that they are all crystalline in nature.

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