

Synthesis and characterization of mixed ligand complexes of Zn(II) and Co(II) with amino acids: Relevance to zinc binding sites in zinc fingers

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Abstract. Mixed ligand complexes of Zn(II) and Co(II) with cysteine, histidine, cysteinemethylester, and histidinemethylester have been synthesized and characterized by elemental analysis, conductivity, magnetic susceptibility measurements, and infrared, ^1H NMR, TGA and FAB mass spectra. In these complexes, histidine, and histidinemethylester act as bidentate ligands involving amino and imidazole nitrogens in metal coordination. Similarly, cysteine, and cysteinemethylester also act as bidentate ligands coordinating through thiol sulphur and amino nitrogen. Tetrahedral geometry has been proposed for Zn(II) and Co(II) complexes based on experimental evidence.

Keywords. Zinc; cysteine; histidine; histidinemethylester; cysteinemethylester.

1. Introduction

The amino acid, histidine, is the most frequently occurring ligand of zinc in the active centre of zinc containing enzymes.¹ Both catalytic and structural zinc in enzymes are always coordinated by at least one cysteine and histidine donor.^{2,3} Of the metal ligating amino acids bearing N, O and S containing donors in their side chains, cysteine and histidine are the most prominent ones for zinc.^{4,5} However, the importance of zinc for stabilization of protein loops in enzymes, zinc fingers etc., has generated new interest in the field of Zn coordination chemistry.^{6–12} The discovery of the ‘zinc fingers’ has triggered intensive research on the interaction of proteins with Zn ions.^{13–18} Zinc complex based units are present in a number of nucleic acid binding and gene regulatory proteins.^{19–22} The transcription factor III A, (TF III A) contains nine tandem repeats of the amino acid motif and each repeat has two invariant cysteines and two invariant histidines coordinated to Zn (Zn-finger).^{23–28} Since zinc is a crucial component of the tertiary structure of TF III A, wherein histidine and cysteine are coordinated to zinc in a tetrahedral configuration, we felt it was important to investigate the interactions of zinc with the corresponding amino acid residues in detail, as a model for the Zn core in TF III A. Since Co(II) ion has been used as an im-

portant spectroscopic probe for proteins that have an N,S (thiolate)-ligated metal centre, such as the ubiquitous zinc finger and blue copper proteins,²⁹ this metal has also been included in this investigation. In our earlier publications, a detailed study regarding the interaction of zinc with histidine, cysteine, histidinemethylester, and cysteinemethylester by pH-metry, ^1H and ^{13}C NMR spectroscopy are reported.³⁰ Further, the factors responsible for the stability of zinc binding domains were assessed. The stability is due to favorable enthalpy and entropy contributions. In view of the importance of these studies, the present work was extended to isolation, characterization and purification of solid complexes involving Zn(II) and Co(II) different metal ions for a comprehensive understanding of binding sites in these systems.

2. Experimental

Cysteine (Cys), histidine (His), cysteinemethylester (Cysme) and histidinemethylester (Hisme) were obtained from the Sigma (USA). AnalaR grade zinc chloride, and cobalt chloride were obtained from E-Merck. They were used as supplied.

2.1 Synthesis of metal complexes

The four complexes $[\text{Zn}(\text{Cys})(\text{His})]^-$ (**1**), $[\text{Co}(\text{Cys})(\text{His})]^-$ (**2**) $[\text{Zn}(\text{Cysme})(\text{Hisme})]^+$ (**3**) and $[\text{Co}$

*For correspondence

(Cysme)(Hisme)]⁺ (**4**) were synthesized by mixing an aqueous solution containing equimolar ratios of Cys (0.001 moles, 0.121 g) and His (0.001 moles, 0.155 g), Cysme (0.001 moles, 0.171 g) and Hisme (0.001 moles, 0.242 g), which were added simultaneously and independently to equimolar concentrations of zinc chloride, and cobalt chloride.

Stoichiometric ratios of metal and ligands are dissolved in aqueous medium and are refluxed until the complex is precipitated, and if not, the pH of the solution mixture is changed to precipitate the complex.

The synthesized complexes were found to be insoluble in the commonly known organic solvents. Consequently, the following physical measurements and analysis were carried out to check the purity and elucidate the structure. All the metal complexes are stable to air and moisture and decompose at very high temperatures.

2.2 Elemental analysis and conductivity data

Carbon, hydrogen and nitrogen analyses were obtained from the microanalytical Heraeus Carlo Erba 1108 elemental analyser. Chloride analysis was carried out by Mohr's method. The metal contents were estimated from these solutions on an atomic absorption spectrometer, Perkin–Elmer 23380. Conductivity of metal complexes was measured in freshly prepared DMSO solutions and obtained using a Digisun Digital conductivity bridge (model: DI-909) and a dip type cell calibrated with KCl solution.

2.3 Spectral analysis

2.3a IR spectra: The IR spectra were recorded (as KBr discs) on infrared spectrophotometers, Shimadzu IR-435, and Perkin–Elmer FTIR in the region 4000–400 cm⁻¹.

2.3b ¹H NMR spectra: Deuterated solutions of [Zn(Cys)(His)] and [Zn(Cysme)(Hisme)] complexes were prepared in 99.8% of D₂O. The pH of the solution was maintained at 5–6 by adding DCl solution. ¹H NMR spectra were recorded for the above complexes of concentration 5 × 10⁻² mol dm⁻³ at room temperature on a Varian Gemini 200/MHz pulsed FT NMR spectrometer. TMS was used as the internal standard. The ¹H NMR spectra for other complexes could not be carried out due to the low solubility of the complexes.

2.3c Reflectance spectra: Reflectance spectra of the complexes were recorded (in KBr discs) on a Shimadzu UV-160 spectrophotometer.

2.3d Magnetic susceptibilities: Magnetic susceptibilities of cobalt complexes were recorded at room temperature on a Faraday balance (CAHN-7600) using Hg[Co(CNS)₄] as the standard. Diamagnetic corrections were made by using Pascal's constants.³¹

2.3e FAB mass spectra: FAB mass spectra of the complexes were recorded using a JEOL SX-120 instrument.

2.4 Thermogravimetric analysis

The absence of coordinated water was established for Zn(II) and Co(II) complexes by thermogravimetric analysis (TGA). TGA was carried out on a Perkin–Elmer model TGS-2 instrument.

3. Results and discussion

Analytical data corresponding to the **1**, **2**, **3** and **4** complexes are compiled in table 1. It may be seen from the table that the complexes are in equimolar stoichiometric 1 : 1 : 1 ratio. The presence or absence of chloride ions in the above complexes was determined by Mohr's method. No evidence was found for the presence of chloride ions in the coordination sphere of the complexes. The conductivity values (table 1) in DMSO correspond to non electrolytes for the complexes.³²

3.1 IR spectra

The aminoacids (His and Cys) exist as zwitterions both in solution and in solid state. The IR spectra of amino acids exhibited significant features in *n*NH₃⁺ *n*COO⁻ regions.³³ In histidine (table 2) the peaks at 3130 cm⁻¹, 3009 cm⁻¹ were assigned to *n*N–H asymmetric and symmetric stretching vibrations. The peak at 2877.3 cm⁻¹ was assigned to *n*C–H stretching frequency. The asymmetric and symmetric stretching vibrations of carboxylate group of histidine were observed at 1588 cm⁻¹ and 1413 cm⁻¹, the peak due to *n* imidazole in-plane was observed at ~964 cm⁻¹. NH₃⁺ twisting and rocking and COO⁻ wagging frequencies were observed in the range 1200–600 cm⁻¹. In cysteine (table 2), the peaks at 3000 cm⁻¹ and

Table 1. Analytical, conductivity and magnetic data of mixed ligand complexes of Zn(II) and Co(II) with cysteine, histidine and cysteinemethyl ester, histidinemethyl ester.

Complex	Found (Calcd) (%)				I_M Ohm ⁻¹ cm ⁻¹ mol ⁻¹ (in DMSO)	μ_{eff} (B.M.) (Temp. K)
	Carbon	Hydrogen	Nitrogen	Metal		
[Zn(Cys)(His)]	31.88	3.80	16.50	19.28	14	Diamagnetic
[ZnC ₉ H ₁₃ N ₄ O ₄ S]	(31.91)	(3.84)	(16.54)	(19.32)		
[Co(Cys)(His)]	32.50	3.87	16.83	17.76	14	3.14 (298)
[CoC ₉ H ₁₃ N ₄ O ₄ S]	(32.53)	(3.91)	(16.87)	(17.75)		
[Zn(Cysme)(Hisme)]	35.78	5.10	15.19	17.69	13	Diamagnetic
[ZnC ₁₁ H ₁₉ N ₄ O ₄ S]	(35.83)	(5.15)	(15.20)	(17.75)		
Co(Cysme)(Hisme)]	36.44	5.18	15.43	(16.21)	13	3.46 (298)
[CoC ₁₁ H ₁₉ N ₄ O ₄ S]	(36.47)	(5.24)	(15.47)	(16.28)		

Table 2. Infrared spectral data of amino acids.

Ligand	$\nu(\text{NH}_3)$		$\nu(\text{COO}^-)$		$\nu(\text{S-H})$	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu(\text{C-O})$
	Asym	Sym	Asym	Sym				
Histidine [C ₆ H ₈ N ₃ O ₂]	3130 (<i>m</i>)*	3009 (<i>m</i>)	1588.8 (<i>m</i>)	1413.7 (<i>s</i>)	–	964.4 (<i>s</i>)	–	–
Cysteine [C ₃ H ₅ NO ₂ S]	3000 (<i>m</i>)	2946 (<i>m</i>)	1582.1 (<i>s</i>)	1404.4 (<i>s</i>)	2600 (<i>sh</i>)	–	–	–
Histidinemethylester [C ₇ H ₁₁ N ₃ O ₂]	3150 (<i>br</i>)	2983 (<i>br</i>)	–	–	–	958.8 (<i>s</i>)	1759 (<i>s</i>)	1290 (<i>s</i>)
Cysteinemethylester [C ₄ H ₈ NO ₂ S]	2986 (<i>m</i>)	2838 (<i>m</i>)	–	–	264 (<i>m</i>)	–	1743 (<i>s</i>)	1245 (<i>s</i>)

**s* = strong; *m* = medium; *w* = weak; *sh* = shoulder; *br* = broad

2946 cm⁻¹ were assigned to $\nu\text{N-H}$ asymmetric and symmetric stretching vibrations. The peak at 2731 cm⁻¹ was assigned to $\nu\text{C-H}$ stretching frequency. The asymmetric and symmetric stretching vibrations of carboxylate group of cysteine were observed at 1582 cm⁻¹ and 1404 cm⁻¹. The peak due to $\nu\text{S-H}$ was observed at 2600 cm⁻¹. The peaks due to νNH_3^+ twisting and rocking and COO^- wagging frequencies were observed in the range 1200–600 cm⁻¹.

The infrared spectra of mixed ligand complexes involving the above ligands showed characteristic band positions, band shifts and band intensities which can be correlated to bidentate amino acids chelation with metal ions.

As regards the chelation of amino acids, the IR spectra exhibited significant features in νNH_2 , νCOO^- regions. It is worthwhile mentioning here that the free amino acids exist as zwitterions (NH_3^+ AA, COO^-) and the IR spectra of these cannot be compared entirely with those of metal complexes as amino acids in metal complexes do not exist as

zwitterions.³⁴ Particularly, free amino acids with NH_3^+ functions shows νNH_3 in the region of 3130–3030 cm⁻¹. In the complexes, NH_3^+ gets deprotonated and binds to metal through the neutral NH_2 group. The transformations of NH_3^+ to NH_2 must result in an upward shift in νNH_2 compared to free amino acids. At isoelectric point, they must show νNH_2 in the region 3500–3300 cm⁻¹. In **1** and **2** complexes (table 3) the IR spectra showed characteristic bands in the region 3300–3000 cm⁻¹ which is lower in comparison with free NH_2 . Hence, it can be concluded that the nitrogen of the amino group is involved in metal coordination. No shift was observed in the asymmetric and symmetric stretching vibrations of carboxylate groups, this supports the non-involvement of carboxylate groups in metal coordination. The spectra also showed shifting of ν imidazole in plane to 1050 cm⁻¹, indicating the coordination of imidazole nitrogen with the metal. The peak due to $\nu\text{S-H}$ is lost in the spectra of the mixed ligand complexes, due to deprotonation of the S–H group on binding

Table 3. Infrared spectral data of mixed ligand complexes of Zn(II) and Co(II) with amino acids.

Ligand	$\nu(\text{NH}_3)$		$\nu(\text{COO}^-)$		$\nu(\text{S-H})$	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu(\text{C-O})$	Non-ligand bands	
	Asym	Sym	Asym	Sym					$\nu(\text{M-N})$	$\nu(\text{M-S})$
[Zn(Cys)(His)] [ZnC ₉ H ₁₃ N ₄ O ₄ S]	3256 (<i>br</i>)*	3150 (<i>br</i>)	1589 (<i>s</i>)	1400 (<i>m</i>)	–	1062 (<i>s</i>)	–	–	500 (<i>m</i>)	400 (<i>m</i>)
[Co(Cys)(His)] [CoC ₉ H ₁₃ N ₄ O ₄ S]	3227 (<i>br</i>)	3120 (<i>br</i>)	1612 (<i>s</i>)	1383 (<i>s</i>)	–	1030 (<i>w</i>)	–	–	470 (<i>m</i>)	410 (<i>w</i>)
[Zn(Cysme)(Hisme)] [ZnC ₁₁ H ₁₉ N ₄ O ₄ S]	3308 (<i>m</i>)	2931 (<i>m</i>)	–	–	–	1069 (<i>m</i>)	1740 (<i>w</i>)	1240 (<i>m</i>)	480 (<i>m</i>)	400 (<i>w</i>)
[Co(Cysme)(Hisme)] [CoC ₁₁ H ₁₉ N ₄ O ₄ S]	3240 (<i>m</i>)	2931 (<i>m</i>)	–	–	–	1090 (<i>m</i>)	1740 (<i>w</i>)	1240 (<i>m</i>)	479 (<i>m</i>)	400 (<i>w</i>)

**s* = strong; *m* = medium; *w* = weak; *sh* = shoulder; *br* = broad

with the metal. The spectra did not show any broad band in the range 3400 cm⁻¹ to 3100 cm⁻¹, indicating the non coordination of water molecules. Other low intensity bands observed in the far IR region in the range 460–500 cm⁻¹ were assigned to $\nu(\text{M-N})$ stretching and 400 cm⁻¹ to $\nu(\text{M-S})$ stretching vibrations. The peak due to $\nu(\text{M-Cl})$ at ~280 cm⁻¹ was not observed, indicating the non coordination of chloride in complexes. Thus from the IR spectra of the mixed ligand complexes it is clear that histidine binds to metal ions through imidazole and amino nitrogens and cysteine binds through thiol sulphur and amino nitrogen.

The IR spectrum (table 2) of esters of amino acids exhibits significant features in $\nu(\text{NH}_3)$ and $\nu(\text{C=O})$ regions. A broad, strong NH₃⁺ stretching band in the 3100–2600 cm⁻¹ region is observed both in the spectrum of histidinemethylester and cysteinemethylester ligands. Multiple combination and overtone bands extend the absorption to about 2000 cm⁻¹. This overtone region usually contains a prominent band near 2222–2000 cm⁻¹ assigned to a combination of the asymmetrical NH₃⁺ bending vibration and a torsional oscillation of the NH₃⁺ group that occurs near 500 cm⁻¹. A weak asymmetric NH₃⁺ bending band near 1660–1610 cm⁻¹ and a fairly strong symmetrical bending band near 1550–1485 cm⁻¹ are observed in the spectra of both ligands. A strong band at 1220–1190 cm⁻¹ arises due to C–C–O stretching and a strong band in the range 1725–1730 cm⁻¹ is assigned to ester carbonyl group. In addition to these bands histidinemethylester has a peak at 958.8 cm⁻¹ due to ν imidazole in plane and cysteinemethylester has a peak at 2641.4 cm⁻¹, due to $\nu(\text{S-H})$ stretching.

In the ternary complexes, the IR spectra (table 3) showed characteristic bands in the region 3300–

3000 cm⁻¹ which is lower in comparison with free $\nu(\text{NH}_2)$ (3500–3300 cm⁻¹). Hence, it can be concluded that the nitrogen of the amino group is involved in coordination with metal. This is also confirmed by the absence of a peak at 2000 cm⁻¹ in the spectrum of metal complexes, due to binding of NH₂ to the metal ion. No shift was observed in the stretching vibration of ester carbonyl group, this supports the non involvement of ester group in metal coordination. The spectra also showed shifting of ν imidazole band to ~1050 cm⁻¹, indicating the coordination of imidazole nitrogen with the metal. The peak due to $\nu(\text{S-H})$ was not seen in the spectra of the mixed ligand complexes, due to deprotonation of the S–H group on binding with the metal. The spectra did not show a broad band in the range 3400 cm⁻¹ to 3100 cm⁻¹, indicating the non-coordination of water molecules. Other low intensity bands observed in far IR region in the range 480–500 cm⁻¹ were assigned to $\nu(\text{M-N})$ stretching and at 400 cm⁻¹ to $\nu(\text{M-S})$ stretching vibrations. The peak due to $\nu(\text{M-Cl})$ at ~280 cm⁻¹ was not observed, indicating the non-coordination of chloride ions in the complexes. Thus from IR spectra of the mixed ligand complexes it is clear that histidinemethylester binds to metal ions with imidazole and amino nitrogens and cysteinemethylester binds through the thiol sulphur and the amino nitrogen atom.

3.2 ¹H NMR spectra

The ¹H NMR assignments at pH 4–5 for free ligands and [Zn(Cys)(His)]⁻ (**1**) complex are summarized in table 4. They were identified with the help of literature data.³⁵ In the ¹H NMR spectra of His, the chemical shifts at 4.02 ppm, 3.29 ppm, 6.97 ppm and 7.71 ppm have been assigned to the resonances due to CH(**a**),

Table 4. $^1\text{H-NMR}$ chemical shifts at pH = 4–5 of cysteine and histidine in the absence and presence of Zn(II).

System	CH(a)	CH ₂ (b)	CH(d)	CH(e)	CH ₂ (b')	CH(a')
Histidine	3.98	3.29	7.01	7.71	–	–
Cysteine	–	–	–	–	3.16	4.06
[Zn(Cys)(His)] [–]	3.6	3.2	7.3	8.55	2.98	3.3

Table 5. $^1\text{H-NMR}$ chemical shifts at pH = 4–5 of cysteinemethylester and histidinemethylester in the absence and presence of Zn(II).

System	CH(a)	CH ₂ (b)	CH(d)	CH(e)	OCH ₃	CH ₂ (b')	CH(a')
Histidinemethylester	4.30	4.04	7.18	8.05	3.38	–	–
Cysteinemethylester	–	–	–	–	3.38	3.28	3.10
[Zn(Cysme)(Hisme)] ⁺	4.28	3.40	7.40	8.62	3.38	3.18	3.03

CH₂(**b**), CH(**d**) and CH(**e**) respectively. In the ^1H NMR spectra of Cys, the chemical shifts at 3.16 ppm and 4.06 ppm have been assigned to the resonances due to CH(**a'**), and CH₂(**b'**) respectively. In the ^1H NMR spectra of the **1** complex, the chemical shifts of histidine corresponding to CH(**e**) and CH(**d**) were shifted downfield and since zinc causes deprotonation of NH₃ protons on binding, the CH(**a**) resonance was shifted upfield. Thus, the spectra confirm the involvement of imidazole and amino nitrogens resulting in a bidentate mode in metal coordination. In cysteine CH₂(**b'**) and CH(**a'**) resonances were shifted upfield in the metal complex, confirming the involvement of thiol sulphur and amino nitrogen atoms in zinc coordination.

The ^1H NMR assignments at pH 4–5 for free ligands and [Zn(Cysme)(Hisme)]⁺ (**3**) complex are summarized in table 5. In the ^1H NMR spectra of Hisme, the chemical shifts at 4.30 ppm, 4.04 ppm, 7.18 ppm, 8.05 ppm and 3.38 ppm have been assigned to the resonances due to CH(**a**), CH₂(**b**), CH(**d**), CH(**e**) and OCH₃ respectively. In the ^1H NMR spectra of Cysme, the chemical shifts at 3.10 ppm, 3.28 ppm and 3.38 ppm have been assigned to the resonances due to CH(**a'**), CH₂(**b'**) and OCH₃ respectively. In the ^1H NMR spectra of the **3** complex, the chemical shifts of Hisme corresponding to CH(**e**) and CH(**d**) were shifted downfield and since zinc causes deprotonation of NH₃ protons on binding, the CH(**a**) resonance was shifted upfield. Thus, the spectra confirm the involvement of imidazole and amino nitrogens in metal coordination resulting in a bidentate mode in metal coordination. In Cysme, CH₂(**b'**) and CH(**a'**) resonances were shifted upfield in the metal complex, confirming the involvement of thiol sulphur

and amino nitrogen atoms in zinc coordination. Thus, the spectra suggest bidentate coordination of these ligands resulting in tetra coordination around zinc.

3.3 Reflectance spectra

The reflectance spectra of the complexes **1** and **2** showed multiple bands at 28820 cm^{–1}, 32790 cm^{–1} and 35210 cm^{–1}, which were assigned to charge transfer (CT) bands in the complexes. However, an additional band at 15380 cm^{–1} was observed in [Co(Cys)(His)][–] complex (figure 1a), which was assigned to *d–d* transition, $^4A_2 \rightarrow ^4T_1(P)$. Accordingly, tetrahedral geometry was proposed for the cobalt complex.

The reflectance spectra of the complexes **3** and **4** showed multiple bands at 28820 cm^{–1}, 32790 cm^{–1} and 35340 cm^{–1}, which were assigned to charge transfer (CT) bands in the complexes. However, an additional band at 15580 cm^{–1} was observed in [Co(Cysme)(Hisme)]⁺ complex (figure 1b), which was assigned to *d–d* transition, $^4A_2 \rightarrow ^4T_1(P)$. Accordingly, tetrahedral geometry was proposed for the cobalt complex.

3.4 Magnetic susceptibility

Magnetic susceptibility are recorded at room temperature on Faraday balance and the magnetic moments of 3.14 BM for **2** and 3.46 BM for **4** complexes suggest that the central metal ion is in high spin configuration. For tetrahedral geometry the magnetic value for spin only moment is 3.89 BM. The values

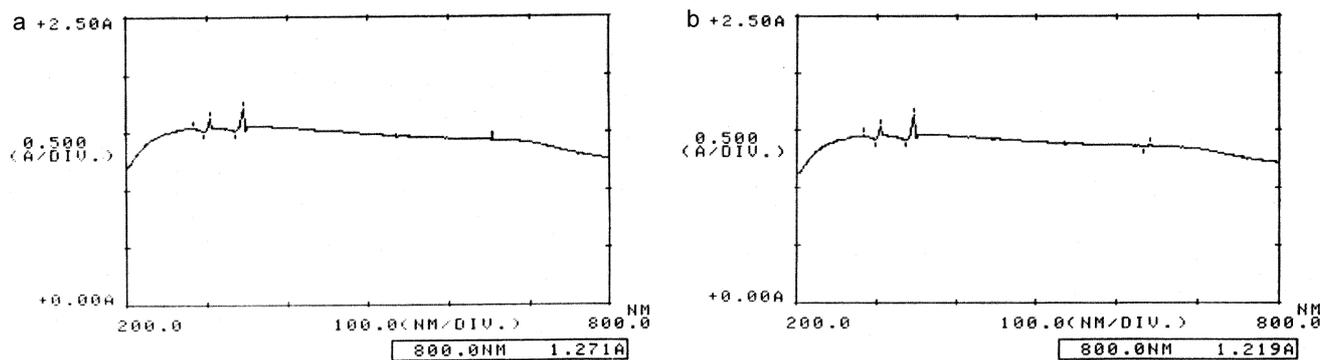


Figure 1. Reflectance spectra of (a) $[\text{Co}(\text{Cys})(\text{His})]^-$ (b) $[\text{Co}(\text{Cysme})(\text{Hisme})]^+$.

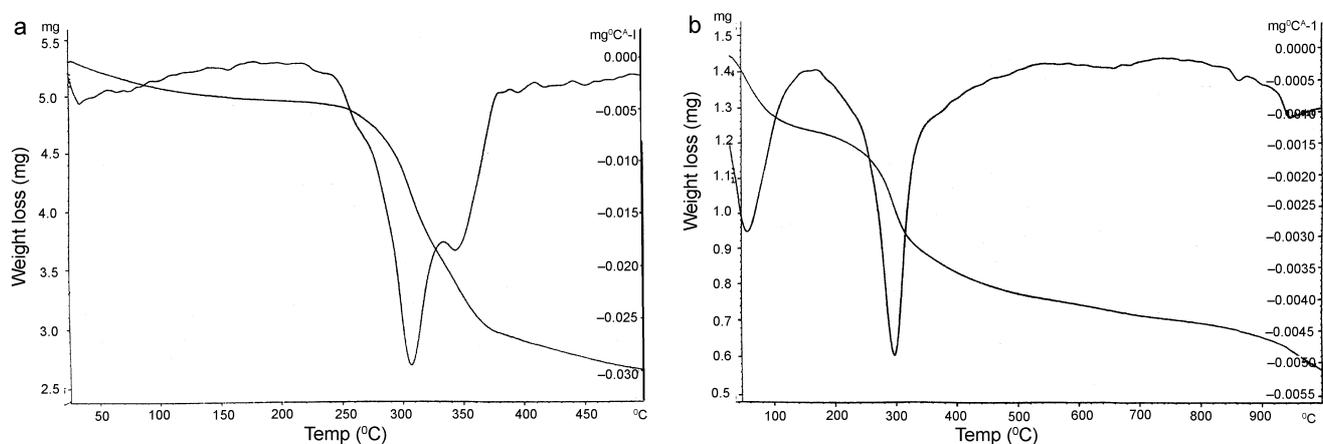


Figure 2. TGA curve of (a) $[\text{Zn}(\text{Cys})(\text{His})]^-$ and (b) $[\text{Co}(\text{Cys})(\text{His})]^-$.

of 3.14 BM and 3.46 BM for the above complexes confirm the tetrahedral geometry.

3.5 Thermogravimetric analysis

The TGA curve of **1** complex (figure 2a) showed the absence of water molecules, as sudden weight loss was observed at 300°C. The total weight loss was 50%. The weight loss at 447°C was 47.9%, which corresponds to a weight loss of molecular weight 160 units. Similarly, the TGA curve of **2** complex (figure 2b) showed absence of water molecules and the total % weight loss is 60.73%, and the weight loss at 891°C was 54.24%, which corresponds to a weight loss of molecular weight of 179 units. The TGA curve of **3** complex showed sudden weight loss at 300°C, indicating the absence of water molecules in the coordination sphere of the complex. The total weight loss was 77.48% and the weight loss at 891°C was 70.15%, which corresponds to a weight loss of molecular weight 257 units. Similarly, the TGA curve

of **4** complex showed the absence of water molecules and the total weight loss was 58.83%, and the weight loss at 891°C was 53.23%, which corresponds to a weight loss of molecular weight of 193 units, implied in a 1 : 1 : 1 complex in accordance with the analytical data.

The thermogravimetric analysis (TGA) provides authentic information regarding the absence of water molecules in the coordination sphere of the complex. Further, the electronic, magnetic, IR and NMR spectral data confirm tetrahedral geometry for all the complexes studied. Based on these conclusions, the structure **2** is proposed for these ternary complexes.

3.6 FAB mass spectra

As an additional support for the above conclusions, the FAB mass spectra of the complexes were recorded (figures 3 and 4). In the FAB mass spectrum (figure 3a) of complex **1**, the molecular ion peak was

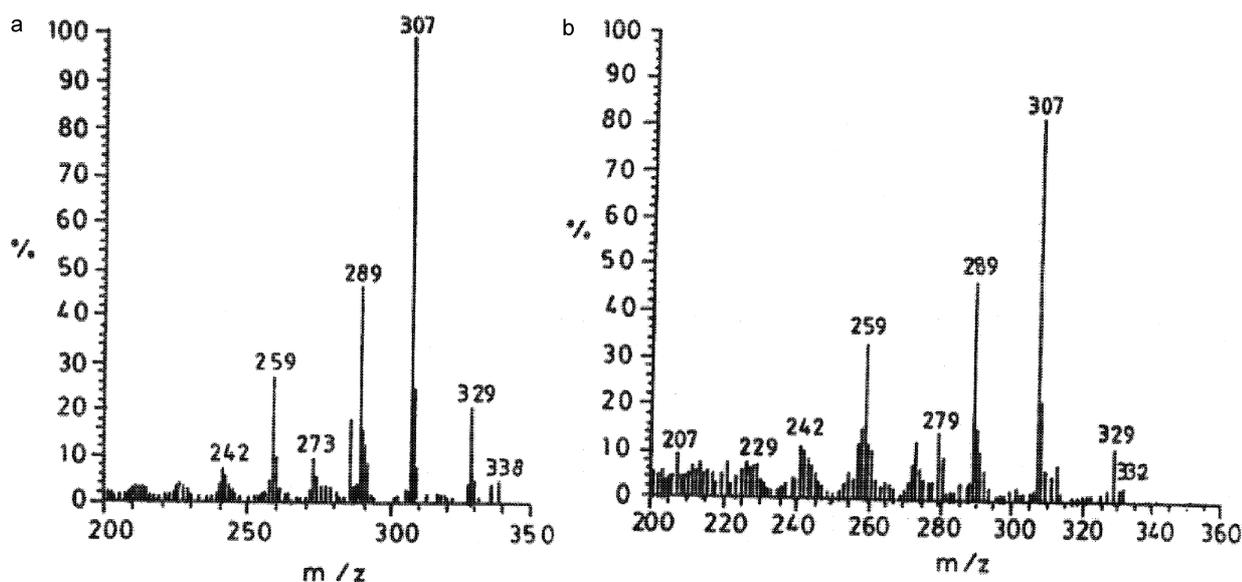


Figure 3. FAB mass spectra of (a) $[\text{Zn}(\text{Cys})(\text{His})]^-$ and (b) $[\text{Co}(\text{Cys})(\text{His})]^-$.

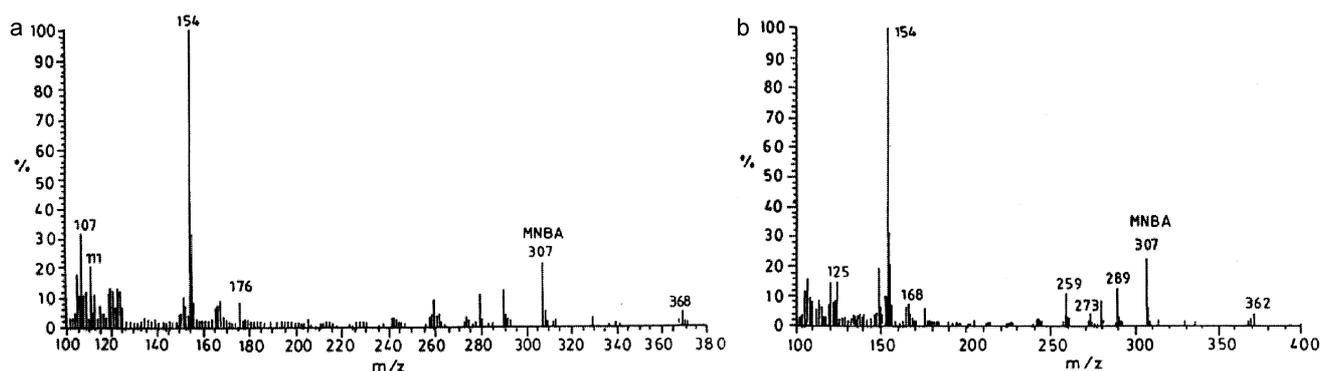


Figure 4. FAB mass spectra of (a) $[\text{Zn}(\text{Cysme})(\text{Hisme})]^+$ and (b) $[\text{Co}(\text{Cysme})(\text{Hisme})]^+$.

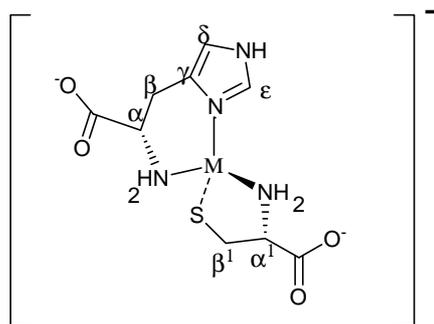
observed at m/z 338, which is in agreement with the molecular weight (338) of the proposed structure. The spectrum showed a peak at m/z 307, which is assigned to *m*-nitro benzyl alcohol. The molecular ion loses S and NH_2 giving an ion at m/z 289. This ion loses one more NH_2 giving an ion at m/z 273, which further loses CH_2 giving an ion at m/z 259. The molecular ion also loses the imidazole ring CH_2 , CH giving a peak at m/z 242.

In the FAB mass spectrum (figure 3b) of complex **2**, the molecular ion peak was observed at m/z 332, which is in agreement with the molecular weight (332) of the proposed structure. The spectrum showed a peak at m/z 307, which is assigned to *m*-nitro benzyl alcohol. The molecular ion loses COO^- giving an ion at m/z 289. The molecular ion also loses $\text{NH}_2\text{-CH-COO}^-$ giving an ion at m/z 259, which fur-

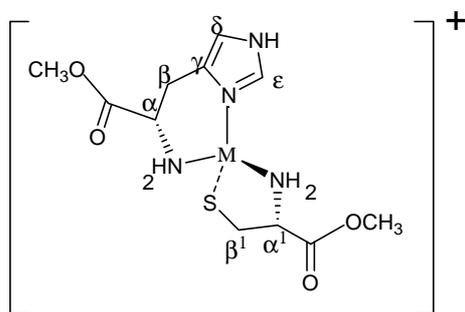
ther loses one more NH_2 giving an ion at m/z 242 and this ion loses CH giving an ion at m/z 229.

In the FAB mass spectrum (figure 4a) of complex **3**, the molecular ion peak was observed at m/z 368, which is in agreement with the molecular weight (368) of the proposed structure. The spectrum shows peaks at m/z 307 and m/z 154, which are assigned to *m*-nitro benzyl alcohol. The molecular ion loses histidinemethylester, $\text{NH}_2\text{-CH-COOCH}_3$ giving an ion at m/z 111. The molecular ion loses imidazole ring, two moles of $(\text{NH}_2\text{-CH-COOCH}_3)$ and CH_2 giving an ion at m/z 176.

In the FAB mass spectrum (figure 4b) of complex **4**, the molecular ion peak was observed at m/z 362, which is in agreement with the molecular weight (362) of the proposed structure. The spectrum showed peaks at m/z 307 and m/z 154, which are assigned to



Structure 1. Geometry of M = Zn (1) and M = Co (2) complexes.



Structure 2. Geometry of M = Zn (3) and M = Co (4) complexes.

m-nitro benzyl alcohol. The molecular ion loses CH-COOCH₃ giving an ion at *m/z* 289. This ion loses NH₂ giving an ion at *m/z* 273, which further loses CH₂ giving ion *m/z* 259. The molecular ion also loses cysteinemethylester, COOCH₃ giving a peak at *m/z* 168, which further loses NH₂, CH, CH₂ giving an ion at *m/z* 125.

Thus the FAB mass spectra further strengthens the proposed structures for [M(Cys)(His)]⁻ and [M(Cysme)(Hisme)]⁺ complexes (structures 1 and 2).

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