Fluoro-metallates : Syntheses, spectral characterization of new mixed-ligand fluoromanganate(III), manganate(II) and fluorozincate(II) complexes containing biogenic co-ligands

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New mixed-ligand fluoro complexes of manganese(III), manganese(II) and zinc(II) containing biogenic co-ligands viz. aspartic acid, glutamic acid, proline, histidine or cysteine have been synthesized from aqueous medium from reaction of freshly prepared $MnO(OH)/Mn(OH)_2/Zn(OH)_2$, 40% HF and the corresponding co-ligands, maintaining molar ratio of 1:4:1 at pH *ca*. 3–6 in presence of alkali metal carbonate, A_2CO_3/alkali metal hydroxide, AOH (A = Na, K or NH_4). Complexes have been precipitated by addition of pre-cooled acetone/ethanol. The compounds are stable in solid state, however, fluoromanganate(III) complexes undergo slow decomposition in aqueous solution. Compounds are practically insoluble in organic solvents such as methanol, ethanol, acetonitrile, dicholomethane and chloroform. The newly synthesized compounds have been comprehensively characterized by chemical analyses, chemical determination of oxidation state of manganese, magnetic susceptibility measurements, FTIR, electronic spectroscopic studies and by TGA/DTA studies.

Keywords: Stabilization, aqueous medium, Mn(III), Mn(II), Zn(II), mixed-ligand fluoro complexes.

Introduction

Amino acids constitute the building blocks of all proteins and enzymes found in nature. It is therefore no surprise that the study of interactions between amino acids and metal centers has attracted the focus of biochemists and bioinorganic chemists for many years, since such interactions are essential for the stability and catalytic activity of metallo-enzymes and metallo-proteins and also for full or partial de-activation of metal free enzyme/proteins upon metal binding[1]. Over the years increasing attention has been paid on the studies of metal-amino acid systems because of their potential as bio-mimetic models[2,3]. Reports on amino acid complexes with manganese compared to those with other transition metal ion are less abundant partly due to their relatively weak interactions. Survey of literature reveals only a handful of structurally characterized manganese amino acid complexes, all of which consists exclusively of manganese(II) centers and majority of them are polymeric in nature[4,5]. Since amino-acids containing complexes with metals such as chromium(III) and iron(III) have been reported[5], we expected the same to be true for manganese (III) given both its

bioinorganic relevance and exciting magnetic properties that many manganese compounds possess[6].

Mixed-ligand complexes containing amino acids as co-ligands are potential biomimetic models for metal-proteins interactions[7]. Amino acids coordination to metals confers unusual structural lability. The geometry, number of ligands, donor groups, nature of binding i.e. micro-coordination environment is the key to the understanding of specific physiological function[8]. Mixed-ligand amino acid complexes are also relevant in enzymes inhibition processes[9]. Pharmacological and toxicological properties of amino acid complexes are another area that has drawn lot of attention[10,11]. Various anions viz. Cl^-, Br^-, SCN^-, NO_3^- have been extensively used as ancillary ligands but use of fluoride as co-ligands are rather sparse. Aqueous medium synthesis of such complexes are also quite complicated as the nature of the complex species formed is often dependent on slight variation in reaction conditions such as concentration of reagents, pH, temperature, and the order of addition of reagents. Despite a long history of metal-amino acid chemistry, the report on mixed-ligand amino acid complexes of manganese(III), manganese(II)

containing fluoride are rather limited[12]. Although few fluoro complexes of zinc(II) with Schiff base ligands are known[13], however, that of zinc(II)-amino acid complexes with fluoride as co-ligands are rather unknown to best of our knowledge.

Thus considering the continued interest in metal amino acid systems and in view of the stabilizing effect of fluoride ion on manganese(II, III) and zinc(II) especially in aqueous medium[14–17], it was therefore considered worthwhile to explore the possibility of synthesizing mixed-ligand fluoro manganese(II), manganese(III) and zinc (II) complexes containing amino acids as co-ligands from aqueous medium. Herein, we report syntheses, characterization, structure assessment and thermal properties of mixed-ligand fluoro complexes of Mn(III), Mn(II) and Zn(II) with amino acids as the ancillary ligands.

Experimental

Chemicals used were all reagent grade products. The compound MnO(OH) was prepared by the oxidation of $Mn(OH)_2$ with hydrogen peroxide[18]. The FT-IR spectra were recorded as KBr discs using a Perkin-Elmer 100 FT-IR spectrometer. Electronic spectra were recorded on a Perkin-Elmer model 1800 spectrophotometer. Magnetic susceptibility measurements were carried out by Gouy method using $Hg[Co(NCS)_4]$ as calibrant. TGA studies were performed using Perkin-Elmer Pyris Diamond model instrument at a heating rate of 5°C/min for the temperature range of 40–1000°C under nitrogen atmosphere.

Synthesis:

(i) Synthesis of mixed-ligand fluoromanganate(III), $A_2[MnF_4(L)(H_2O)]$ (L = aspartic acid, A = Na, K, NH_4; L = glutamic acid, A = Na, K); $A[MnF_4(L)(H_2O)]$ (L = histidine, A = Na; L = proline, A = Na, K) and $A_2[MnF_4(L)].H_2O$ (L = cysteine, A = Na).

As the method of synthesis of the complexes are similar, a general method is given.

An aqueous suspension (20 cm^3) of freshly prepared 0.89 g (10.00 mmol) of MnO(OH) was dissolved in 2.0 cm^3 (40.00 mmol) of 40% HF with continuous stirring. The solution was stirred for *ca*.10 min followed by addition of an aqueous solution of amino acid (10.00 mmol, 1.33 g aspartic acid/1.47 g glutamic acid/1.15 g proline/1.55 g histidine/1.21 g cystiene) and the solution was further stirred for a period of *ca.* 20 min. To the resultant mixture solid A_2CO_3/AOH solution (A = Na,

K, NH_4) was added with stirring keeping the MnO(OH):AOH/ A_2CO_3 ratio as 1:1. Slow addition of pre-cooled acetone/ethanol led to the precipitation of pink microcrystalline compounds. The compounds were separated by filtration, washed 3-4 times with small volume of acetone/ethanol and dried *in vacuo* over conc. H_2SO_4.

(ii) Synthesis of mixed-ligand fluoromanganate(II), $A_3[Mn(L)F_4].2H_2O$ (L = glutamic acid, A = K); $A_3[Mn(L)F_4].2H_2O$ (L = aspartic acid, A = K); $A_2[Mn(L)F_4].2H_2O$ (L = histidine, A = K).

An aqueous suspension (25 cm^3) of freshly prepared $Mn(OH)_2$ 0.88 g (10.11 mmol) was dissolved in 2.0 cm^3 40% HF (40.0 mmol) and stirred for *ca.* 10 min. To the clear the solution added (10.0 mmol) of amino acids (L), glutamic acid (1.33 g)/aspartic acid (1.33 g)/histidine (1.33 g), maintaining $Mn(OH)_2$:L:HF ratio at 1:1:4. After stirring the reaction mixture for *ca.* 5 min, solid of K_2CO_3 was added in small portion maintaining $Mn(OH)_2$:K_2CO_3 ratio as 1:1 and whole was stirred for further period of *ca.* 10 min. To the resultant solution added an equal volume of pre-cooled ethanol, when light pink microcrystalline solid separated out. Compounds were collected by filtration, washed 3-4 times with small volume of ethanol and dried *in vacuo* over conc. H_2SO_4.

(iii) Synthesis of mixed-ligand fluorozincate(II), $A_2[Zn(L)F_4(H_2O)].2H_2O$ (L = glutamic acid, A = K) and $A_2[Zn(L)F_4(H_2O)]$ (L = histidine, A = K).

An amount of 1.0 g (10.0 mmol) of freshly prepared zinc hydroxide was dissolved in 40% HF (2.0 cm^3, 40.0 mmol) and stirred for *ca.* 10 min. To the clear solution added 10.00 mmol of glutamic acid (1.47 g)/histidine (1.55 g) keeping $Zn(OH)_2$:L:HF ratio at 1:1:4. The pH of the reaction mixture was adjusted to *ca.* 6.5 by slow addition of aqueous (2 N) KOH solution. Pre-cooled ethanol was added to the reaction mixture, whereupon white microcrystalline products separated out. Compounds were filtrated in suction, washed with small volume of ethanol and dried *in vacuo* over conc. H_2SO_4.

Elemental analyses:

Manganese was estimated volumetrically by complexometric titration with EDTA[19] using Erio-T as indicator. The fluoride contents of the compounds were determined by Volhard's method[20]. Sodium, potassium were determined by the method reported in literature[21]. Carbon, hydrogen and nitrogen were estimated by micro-analytical methods (Analytical data are given in Table 1).

Table 1. Analytical data for the complexes

Compound	Yield (%)	Found (Calcd.) (%)					
		A	Mn	F	C	H	N
$Na_2[MnF_4(L)H_2O]$	76	14.16	16.83	23.27	14.71	2.18	4.30
(L = aspartic acid)		(14.11)	(16.81)	(23.24)	(14.78)	(2.16)	(4.29)
$(NH_4)_2[MnF_4(L)H_2O]$	78	–	17.38	23.99	15.20	4.76	13.30
(L = aspartic acid)			(17.35)	(23.89)	(15.29)	(4.78)	(13.26)
$Na_2[MnF_4(L)H_2O]$	74	13.54	16.10	22.32	17.68	2.65	4.10
(L = glutamic acid)		(13.51)	(16.12)	(22.28)	(17.75)	(2.61)	(4.11)
$K_2[MnF_4(L)H_2O]$	75	20.93	14.72	20.39	16.14	2.45	3.78
(L = glutamic acid)		(20.89)	(14.74)	(20.35)	(16.19)	(2.43)	(3.76)
$Na[MnF_4(L)(H_2O)]$	71	14.08	16.85	23.27	18.38	3.64	4.29
(L = proline)		(14.06)	(16.82)	(23.24)	(18.34)	(3.66)	(4.31)
$K[MnF_4(L)(H_2O)]$	73	21.69	15.31	21.14	16.69	3.37	3.89
(L = proline)		(21.72)	(15.34)	(21.16)	(16.71)	(3.34)	(3.92)
$Na[MnF_4(L)(H_2O)]$	80	7.09	16.84	23.33	22.10	2.81	12.91
(L = histidine)		(7.05)	(16.87)	(23.31)	(22.08)	(2.78)	(12.88)
$Na_2[MnF_4(L)].H_2O$	76	14.62	17.48	24.14	11.40	2.27	4.46
(L = cysteine)		(14.60)	(17.46)	(24.12)	(11.42)	(2.24)	(4.44)
$K_3[Mn(L)F_4].2H_2O$	72	30.78	14.47	19.99	12.62	1.31	3.68
(L = aspartic acid)		(30.67)	(14.42)	(19.96)	(12.58)	(1.29)	(3.65)
$K_3[Mn(L)F_4].2H_2O$	65	29.69	13.95	19.28	15.22	1.77	3.55
(L = glutamic acid)		(29.56)	(13.89)	(19.24)	(15.18)	(1.73)	(3.49)
$K_2[Mn(L)F_4].2H_2O$	71	29.10	13.68	18.90	17.90	1.74	3.48
(L = histidine)		(29.14)	(13.63)	(18.85)	(17.86)	(1.69)	(3.44)
$K_2[Zn(L)F_4(H_2O)].2H_2O$	70	18.66	14.63	3.82	18.61	3.44	15.81
(L = glutamic acid)		(18.59)	(14.58)	(3.76)	(18.54)	(3.37)	(15.76)
$K_2[Zn(L)F_4(H_2O)]$	66	19.94	20.18	3.71	18.03	10.80	16.51
(L = histidine)		(19.83)	(20.12)	(3.66)	(18.10)	(10.71)	(16.46)

Chemical determination of oxidation state of trivalent manganese:

The oxidation state for manganese in compounds containing trivalent manganese was determined iodometrically by treating a freshly prepared ice-cold potassium iodide solution, acidified with dilute sulfuric acid, with the compound followed by titration of the liberated iodine against a standard sodium thiosulfate solution.

Results and discussion

As emphasized (*vide infra*) metal complexes containing amino acids as co-ligands are potential bio-mimetic models for many biochemical processes and the physiologically interesting mixed-ligand complexes of amino acids with metal ions play important role in biological systems have been a subject of great interest. Despite a long history of metal-amino acid chemistry, reports on manganese amino acid complexes containing fluoride as ancillary ligands are rather limited (*vide infra*). It was therefore rational to consider that mixed-fluoro complexes of manganese in di and trivalent states containing different amino acids viz. aspartic acid, glutamic acid, histidine, proline and cysteine could be stabilized in solution by maintaining proper reaction condition and can be isolated in the solid state to get an access to host of mixed-ligand manganese complexes. Similarly, information on mixed-ligand complexes of zinc with biogenic ligands like amino acids containing fluoride as co-ligand is also very limited.

Accordingly, synthetic strategy was chalked out and syntheses of host of mixed-ligand fluoro manganese(II), manganese(III) and zinc(II) complexes containing amino acids viz. aspartic acid, glutamic acid, proline, histidine and

cysteine as biogenic co-ligands were accomplished from the reaction of freshly prepared $MnO(OH)/Mn(OH)_2/Zn(OH)_2$, 40% HF and the corresponding amino acids ($Mn:F^-:$amino acid ratio as 1:4:1) at pH ~3–6 in presence of A_2CO_3 or AOH solution (A = Na, K, NH_4). An excess amount of fluoride was avoided in the reaction solution in order to suppress the formation of $[MnF_5]^{2-}$ or $[ZnF_4]^{2-}$ instead of the desired compounds. Slow addition of pre-cooled acetone or ethanol to the reaction mixture facilitated precipitation of the compounds in reasonably good yield. The compounds synthesized in this way were found to be microcrystalline products, sparingly soluble in water and practically insoluble in organic solvents viz. ethanol, methanol, acetonitrile, dicholometane and chloroform. The compound are stable in absence of moisture can be stored in sealed polythene bags for prolonged period. Due to poor solubility single crystals of the compounds could not be isolated for X-ray diffraction studies even after several attempts.

Magnetic measurements:

The results of room temperature (300 K) magnetic susceptibility measurements of the fluoro manganate(III) complexes exhibit magnetic moment values in the range 4.8 to 5.1 B.M. The observed values are normal for high spin d^4 system of Mn(III) occurring in an octahedral or a distorted octahedral environment. In case of fluoromanganate(II) complexes the observed magnetic values are 5.37–5.42 B.M. as expected for a high spin d^5 system. The fluorozincate(II) complexes are diamagnetic nature.

Electronic spectra:

The electronic spectra of fluoromanganate(III) complexes exhibit similar features in terms of their position, pattern and intensities of the observed bands. The electronic spectra of freshly prepared complexes were recorded immediately after making an aqueous solution(10^{-5} M) containing very small amount of 40% HF. $A_2[MnF_4(L)(H_2O)]$ (L = aspartic acid) exhibit bands at *ca.* 25,000 cm^{-1}, *ca.* 19,200 cm^{-1} and *ca.* 14,700 cm^{-1}. The observed bands are assignable to $^5B_{1g}{\rightarrow}^5E_g$, $^5B_{1g}{\rightarrow}^5B_{2g}$ and $^5B_{1g}{\rightarrow}^5A_{1g}$ modes of transitions respectively[22]. Absorptions for $A_2[MnF_4(L)(H_2O)]$ (L = glutamic acid), were observed at *ca.* 25,000 cm^{-1} and *ca.*19,200 cm^{-1}, assigned as $^5B_{1g}{\rightarrow}^5E_g$ and $^5B_{1g}{\rightarrow}^5B_{2g}$ transitions; whereas $A[MnF_4(L)(H_2O)]$ (L = proline), absorption bands were observed at *ca.* 22,200 cm^{-1} and *ca.* 15,800 cm^{-1}, due to $^5B_{1g}{\rightarrow}^5B_{2g}$ and $^5B_{1g}{\rightarrow}^5A_{1g}$ modes of transi-
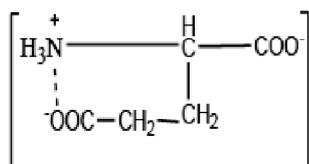
tions. The observed spectral pattern is quite characteristic of the presence of high spin manganese(III) ion in each of the compounds and suggest an appreciable splitting of ^5E_g ground state of manganese(III), leading to a distorted octahedral environment around manganese(III) centre in the complex species[22]. Appearance of higher energy bands in the region (41,600–33,300 cm^{-1}) in all the synthesized manganese(III) complexes may be attributed to charge transfer transitions. Due to poor solubility of the Mn(II) and Zn(II) complexes, suitable absorption spectra of the complexes in aqueous solution could not be recorded.

Infrared spectra:

The infrared spectroscopy furnishes interesting and useful information regarding the interactions of amino acids with metal ions. The ligand itself, in absence of the metal ion, may exhibit a spectrum which varies with the pH i.e. the spectra of acid and the conjugate base form of the ligand may differ significantly. The infrared spectra of the complexes display pattern typical of coordinated amino acids and fluoride ligands. The carboxylate (COO^-) stretching frequencies of amino acids are affected by coordination as well as by intermolecular interactions with the increase in asymmetric (COO^-) stretching frequency while symmetric ones are shifted to lower values[23]. These differences in the position of $v_{asy}(COO^-)$ and $v_{sym}(COO^-)$ stretching vibrations of the free acids and the complexes are consistent with the coordination of carboxylic group. The $\Delta v(COO^-)$ values for the complexes were greater than the $\Delta(COO^-)$ values found for the free amino acids. Such increase in the values of $\Delta v(COO^-)$ are typical of monodentate coordination of the amino acids[24].

Infrared spectra of complexes containing Mn(III) ions displayed sufficiently well resolved spectral patterns. The mode of coordination of glutamic and aspartic acids to a metal centre can be ascertained by careful examination of IR spectra of such compounds. Generally, two strong absorption peaks for (COO^-) moiety at *ca.* 1705 and 1630 cm^{-1} are observed when the amino acids is coordinated to metal in tridentate fashion involving both the carboxylate group and amino nitrogen, while one strong (COO^-) stretching band at 1620 cm^{-1} is observed if amino acids act in bidentate manner ligating through one of its carboxylate group and amino nitrogen atom[25]. Involvement of the -NH_2 group in coordination also causes a shift of the N-H stretching frequency to lower energy[25,26]. The notable features of the IR spectra of

$A_2[MnF_4(L)(H_2O)]$ (L = aspartic acid) are absorptions bands at *ca.* 1501–1508 cm^{-1}, 1310–1318 cm^{-1} assigned as $\nu_{asy}(COO^-)$ and $\nu_{sym}(COO^-)$ modes of vibrations. The differences of frequencies between $\nu_{asy}(COO^-)$ and $\nu_{sym}(COO^-)$, $\Delta\nu$, was higher than that observed for the free acid and indicative of monodentate coordination of carboxylate group. Appearance of bands in the range 1619–1639 cm^{-1} and 1423 cm^{-1} were attributed to $\delta_d(NH_3^+) + \delta(H_2O)$ and $\delta_s(NH_3^+)$ modes of vibrations of zwitterionic form of the amino acid[27]. Absence of any band at *ca.* 1700 cm^{-1} due to $\nu(COOH)$, suggest the nonexistence of non-ionized carboxylic groups in these complexes. One of the deprotonated carboxylate groups may be involved in hydrogen bonding interaction with the protonated -NH$_2$ group of the zwitterionic form of the amino acid. The relatively unaltered position of $\nu(NH)$ *ca.* 3140 cm^{-1} associated with protonated amino group further support coordination of amino acid through carboxylate oxygen. Absence of bands due to $\nu(Mn-N)$ and $\delta(Mn-N)$ suggests, aspartic acid is present in its zwitterionic form and

$$\begin{bmatrix} \overset{+}{H_3N} \!\!-\!\!-\!\!-\!\!-\!\! \overset{\overset{H}{|}}{\underset{|}{C}} \!\!-\!\! COO^- \\ {}^-OOC-CH_2-CH_2 \end{bmatrix}$$

coordinated by one of its carboxylate oxygen in monodentate fashion. Appearance of strong band at *ca.* 567–580 cm^{-1} originate from the presence of coordinated fluoride and is attributed to $\nu(Mn-F)$[28]. A medium intensity band at *ca.* 475–478 cm^{-1} was assigned to $\nu(Mn-O)$. The broadening of this band suggest that the fluoride probably occupy *cis* position around the manganese(III) centre. From observed position of $\nu(OH)$ at 3421 cm^{-1}, no clear inference can be made regarding the nature of water molecule, however, appearance of a distinct band at 743 cm^{-1} due to rocking mode of vibration of water molecule provide evidence for the existence of coordinated water molecule in the complexes[29]. TGA data also support the notion of nonexistence of lattice water in the complexes under discussion (*vide-supra*).

The infrared spectral features of $A_2[MnF_4(L)(H_2O)]$ (L = glutamic acid, A = Na, K) are very similar to that of aspartatofluoromanganate(III) complexes as discussed above. The glutamatofluoromagnate(III) complexes exhibit bands similar to that of aspartato complexes at *ca.* 1509 cm^{-1},

1354 cm^{-1}, 1650–1655 cm^{-1}, 1423 cm^{-1}, 744 cm^{-1}, 590 cm^{-1}, 482 cm^{-1} and *ca.* 3463 cm^{-1}, which owe their origin to $\nu_{asy}(COO^-)$, $\nu_{sym}(COO^-)$, $\delta_d(NH_3^+) + \delta(H_2O)$, $\delta_s(NH_3^+)$, $\rho_r(H_2O)$, $\nu(Mn-F)$, $\nu(Mn-O)$ and $\nu(OH)$ modes of vibrations respectively. Thus the IR spectral data also suggests that glutamic acid is also coordinated to the manganese(III) centre through its carboxylate oxygen atom. The observed $\Delta\nu(COO^-)$ value in this case is also greater than that of free acids and indicative of monodentate coordination of carboxylate group as observed for the aspartato complexes. Existence of zwitterionic form of the glutamic acid suggest non participation of nitrogen atom of amino group in coordination, which is further supported by absence of bands at *ca.* 450 and *ca.* 350 cm^{-1} due to $\nu(Mn-N)$ and $\delta(Mn-N)$ modes of vibrations. Coordinated water molecule is evidenced by the occurrence of a typical band at to $\rho_r(H_2O)$ at 744 cm^{-1} due to rocking mode of water.

Fluoromanganate(II) complexes containing glutamate, aspartate as co-ligand, FT-IR spectra show strong absorptions at *ca.* 1589–1605 cm^{-1}, 1355–1364 cm^{-1} assigned as $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes of vibrations. The difference of frequencies between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ in this cases is also higher than the free amino acids and support the monodentate coordination of carboxylate group. Appearance of bands in the range *ca.* 1644 and 1421–1429 cm^{-1} are attributable to $\delta_d(NH_3)$ and $\delta_s(NH_3^+)$ of zwetterionic form of amino acid. Absence of any band around 1700 cm^{-1} indicates absence of non-ionized carboxylate group (-COOH) in the compounds. Relatively unaltered position of $\nu(N-H)$ at *ca.* 3068–3199 cm^{-1} associated with protonated amino group further support coordination of amino acids through their carboxylate oxygen. A strong band in the region *ca.* 551–553 cm^{-1} originate from the presence of $\nu(Mn-F)$ of coordinated fluoride.

Mixed-ligand fluorozincate(II) complexes also exhibit sufficiently well resolved spectral pattern due to coordinated amino acid and fluoride ligand. IR spectrum of $A_2[Zn(L)F_4(H_2O)].2H_2O$ (L = glutamic acid) show prominent bands at *ca.* 1591 and 1406 cm^{-1} due to vibrations of carboxylate group. The difference of frequency between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ ($\Delta\nu$) greater than 200 cm^{-1} as observed for other compounds suggest monodentate coordination of carboxylate group of amino acid. However, appearance of a strong band at ~1730 cm^{-1} is assignable to

the existence of a non-ionized carboxylic (COOH) group in the compound. Additional bands at *ca.* 1625 and 1467 cm^{-1} are attributable to $\delta_d(NH_3^+)$ + $\delta(H_2O)$ and $\delta_s(NH_3^+)$ vibrations of zwitterionic form of amino acid as also observed for manganese complexes. Relatively unaltered position of ν(N-H) at 3440 cm^{-1} associated to the protonated amino group indicate non participation of NH$_2$ group in coordination. Strong band at 625 cm^{-1} originate from the presence of coordinated fluorides and attributed to ν(Zn-F)[28]. A medium intensity band at 352–372 cm^{-1} assigned to ν(Zn-O) vibration. Here again from the observed position of ν(OH) at 3445 cm^{-1}, no clear inference can be drawn regarding the nature of water molecule, however, appearance of a band at *ca.* 758 cm^{-1} due to rocking mode of vibration of water molecule provide evidence for the existence of coordinated water. TGA data of the compounds also support the existence of both coordinated water and lattice water in the complex under discussion.

The infrared spectra of fluromanganate(III) containing proline as co-ligand are informative. The significant features of the IR spectra of A[MnF$_4$(L)(H$_2$O)] (L = proline) show absorptions due to coordinated proline and fluoride. The $\nu_{asy}(COO^-)$ was observed at *ca.* 1659 cm^{-1} and the corresponding symmetric stretching $\nu_{sym}(COO^-)$ vibration appeared at 1385 cm^{-1}. The differences between asymmetric and symmetric stretching vibrations of carboxylate groups (< 200 cm^{-1}) in this case also suggest the coordination of carboxylate oxygen in monodentate fashion. Absence of any band at *ca.* 1700 cm^{-1} indicates the deprotonation of the carboxylic acid group (COOH). The appearance of a band at *ca.* 751 cm^{-1} assignable to rocking mode, $\rho_r(H_2O)$ of water suggest existence of coordinated water. Strong band at *ca.* 480 cm^{-1} is due to ν(Mn-F), of coordinated fluoride.

A comparison of IR spectra of histidine complex with that of free acid provides useful information about the mode of coordination of histidine. Coordination of histidine to the metal centre is largely depends on the pH condition of the reaction medium[30]. Monodentate coordination through carboxylate oxygen occurs at pH *ca.* 2.75, when amino group is completely protonated. Bidentate coordination occurs at pH *ca.* 5, whereas, tridentate coordination involving carboxylate oxygen, amino nitrogen and imidazole ring nitrogen takes place above pH 11. The involvement of imidazole group of histidine in coordination usually takes place at a higher pH value

than the carboxylate group, but at a lower value than that of amino group. In FTIR spectrum of A[MnF$_4$(L)(H$_2$O)] (L = histidine,) prominent bands at *ca.* 1500–1550 and 1300–1344 cm^{-1} are assigned as $\nu_{asy}(COO^-)$ and $\nu_{sym}(COO^-)$ vibrations respectively. The shifting of carboxylate stretching frequencies in the complexes with respect to those observed for free acid (1579 cm^{-1} and 1412 cm^{-1}) is typical of carboxylate coordination and the differences between these modes, more than 200 cm^{-1} is again typical of monodentate coordination of carboxylate group as expected considering the fact that synthesis was carried out in highly acidic condition (pH ~3). Absence of any band at *ca.* 1700 cm^{-1} suggests deprotonation of the carboxylate moiety. The absorptions at *ca.* 1602 cm^{-1} and at *ca.* 1411 cm^{-1} have been assigned to $\delta_d(NH_3^+)$ + $\delta(H_2O)$ and $\delta_s(NH_3^+)$ modes of vibrations, indicating histidine exists in zwitterionic form and rule out the possibility of coordination of nitrogen atom of amino group to the metal centre. Participation of imidazole ring in coordination is not expected considering the highly acidic conditions of the reaction medium. Absence of any band due to ν(Mn-N) also support the idea of non-involvement of nitrogen atom in coordination. Thus IR data unequivocally suggest monodentate coordination of histidine to the manganese(III) centre. Medium intensity band at 499 cm^{-1} in the spectrum was assigned to ν(Mn-F) of coordinated fluoride. Here again, band at *ca.* 781 cm^{-1} has been assigned as rocking mode of vibration, $\rho_r(H_2O)$ of coordinated water as observed in cases of other complexes discussed earlier.

The IR spectrum of histidinefluoromanganate(II) complex also show a number of bands and assignment was done by careful comparison of IR spectra of the compound with that of the free histidine. The notable features of the IR spectrum of the complex are bands at *ca.* 1638 cm^{-1}, 1336 cm^{-1}, 1498 and 1414 cm^{-1} are assigned as $\nu_{as}(COO^-)$, $\nu_s(COO^-)$, $\delta_d(NH_3)$ and $\delta_s(NH_3^+)$ modes of vibrations respectively. The terminal mode of coordination of fluoride was ascertained from appearance of bands in the region 631–530 cm^{-1}. For flurozincate(II) histidine complexes, A$_2$[Zn(L)F$_4$(H$_2$O)] (L = histidine), the infrared spectra show prominent bands at *ca.* 1590 and *ca.* 1355 cm^{-1} which are assigned as $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes of vibrations. The shifting of carboxylate stretching frequencies in the complex with respect to those of the free acid supports carboxylate coordination to zinc(II) centre. The $\Delta\nu$ [$\nu_{asy}(COO^-) - \nu_{sym}(COO^-)$], > 200 cm^{-1} due to a monodentate coordination of carboxylate group.

Table 2. Significant IR spectral bands (cm^{-1}) and their assignments

| Complexes	$\nu(OH)$	$\nu_{asy}(COO^-)$	$\nu_{sym}(COO^-)$	$\delta_d(NH_3^+)$	$\delta_s(NH_3^+)$	$\rho_r(H_2O)$	$\nu(Mn\text{-}F)/$ $\nu(Zn\text{-}F)$	$\nu(Mn\text{-}O)/$ $\nu(Zn\text{-}O)$
$A_2[MnF_4(L)(H_2O)]$ (L = aspartic acid)	3421–3463	1501–1508	1310–1318	1619–1639	1423	743	567–590	475–478
$A_2[MnF_4(L)(H_2O)]$ (L = glutamic acid)	3463	1509	1354	1650–1655	1423	744	590	482
$A[MnF_4(L)(H_2O)]$ [L = proline]	3459	1639–1659	1385			744–746	483–497	414
$A[MnF_4(L)(H_2O)]$ [L = histidine, A = Na]	3414	1500–1550	1344	1602	1411	781	499	490
$A_2[MnF_4(L)].H_2O$ (L = cysteine, A = Na)	3418	1660	1384	1593	1450		467	467
$A_3[Mn(L)F_4].2H_2O$ (L = aspartic acid, A = K)	3435	1589	1355	1644	1421		551	490
$A_3[Mn(L)F_4].2H_2O$ (L = glutamic acid, A = K)	3445	1605	1364	1644	1429		553	463
$A_2[Mn(L)F_4].2H_2O$ (L = histidine, A = K)	3430	1638	1336	1498	1414		631–530	481
$A_2[Zn(L)F_4(H_2O)].2H_2O$ (L = glutamic acid, A = K)	3445	1591	1406	1625	1467	758	625	352–372
$A_2[Zn(L)F_4(H_2O)]$	3440	1590	1355	1644	1421	810	415–539	414

Deprotonation of the carboxylate group was assumed from absence of any bands at *ca.* 1700 cm^{-1}. The absorptions at 1644 cm^{-1}, 1421 cm^{-1} are assigned to $\delta_d(NH_3^+)$ + $\delta(H_2O)$ and $\delta_s(NH_3^+)$ modes, zwitterionic form of histidine and rule out the possibility of coordination of nitrogen of amino group. Synthesis of the complex was carried out at pH *ca.* 3 thus participation of imidazole ring is not expected. Absence of any band assignable to $\nu(Zn\text{-}N)$ also supports the idea. Appearance of strong band at 415 cm^{-1} and a shoulder at 539 cm^{-1} in the spectrum were assigned to $\nu(Zn\text{-}F)$ arising from the occurrence of coordinated fluoride. Rocking mode of vibration, $\rho_r(H_2O)$ of coordinated water was observed as medium intensity band at 810 cm^{-1}.

In case of fluoromanganate(III) cysteine complex, $A_2[MnF_4(L)].H_2O$, coordination of carboxylate oxygen is evidenced by the observed asymmetric carboxylate stretching, at 1660 cm^{-1} and the corresponding symmetric stretching at 1384 cm^{-1}. The IR spectrum did not show $\nu(S\text{-}H)$ absorption at 2568 cm^{-1}, suggesting coordination of sulphur atom of cysteine to the manganese(III)[31]. The existence of NH_3^+ group is characterized by the doublet arising from the symmetric and degenerate bending modes at *ca.* 1450 cm^{-1} and 1593

cm^{-1} respectively. Appearance of additional bands in the region 718–1211 cm^{-1} are due to NH_3^+ rocking, CH_2 rocking, C-N, C-C stretching modes. IR spectral data thus unequivocally suggest bidentate coordination of cysteine involving its carboxylate oxygen and cystenyl sulphur. Terminal coordination of fluoride was ascertained from the appearance of medium intensity band at 467 cm^{-1}. A broad band at *ca.* 3418 cm^{-1} is assignable to $\nu(OH)$ of the lattice water, however, the corresponding bending vibration $\delta(HOH)$ could not be ascertained and probably had merged with the asymmetric carboxylate stretching vibration. Thus IR spectral data for the complexes as discussed provided very useful information regarding the mode of bonding of ligands in the complexes under discussion.

Thermogravimetric studies:

Thermogravimetric analyses (TGA/DTA) were carried out to ascertain the thermal stability of the complexes. The results of thermogravimetric analysis of $A_2[MnF_4(L)(H_2O)]$ (L = aspartic acid) shown, the first endothermic process peak at 239°C, correspond to the loss of two molecules of HF (obsd. loss, 11.79%; calcd. 12.2%). Further weight losses of 9.45%, 10.77% and 4.94% were observed in the temperature range
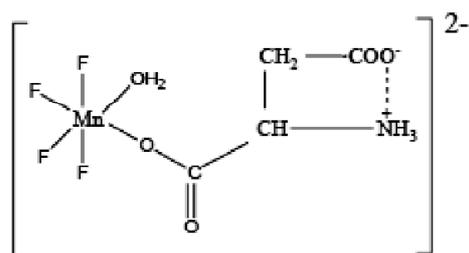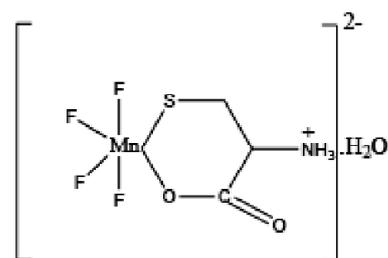
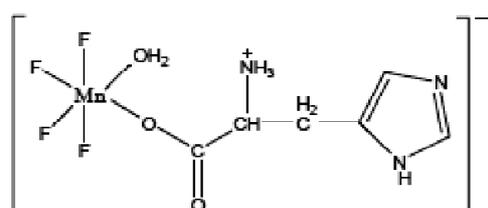$A_2[MnF_4(L)(H_2O)]$ (L=aspartic acid, A=Na, NH_4)
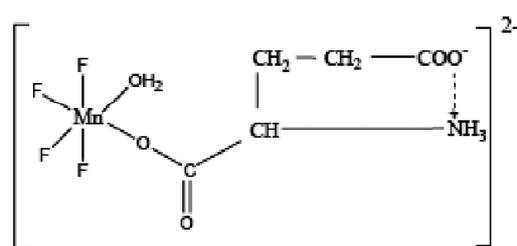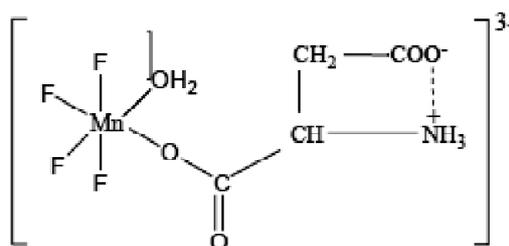
$A_2[MnF_4(L)(H_2O)]$ (L=glutamic acid, A=Na, K)
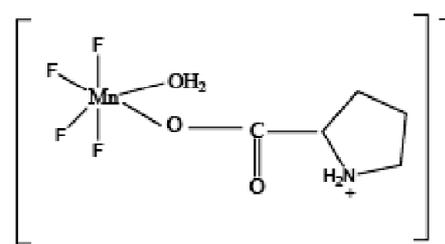
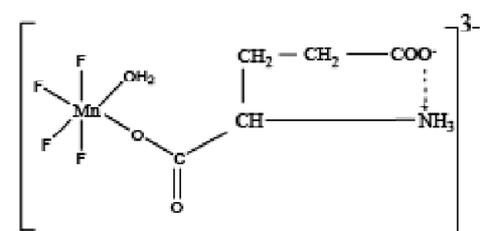$A[MnF_4(L)(H_2O)]$ (L=proline, A=Na, K)

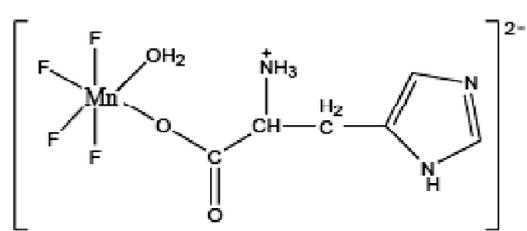$A_2[MnF_4(L)(H_2O)]$ (L=cysteine, A=Na)

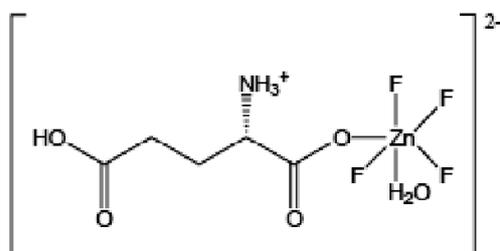$(A[MnF_4(L)(H_2O)]$ A=Na and L=histidine)
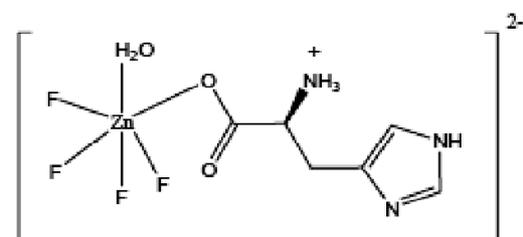
$A_3[MnF_4(L)(H_2O)]$ (L=aspartic acid, A=K)

$A_3[MnF_4(L)(H_2O)]$ (L=glutamic acid, A=K)

$A_2[MnF_4(L)(H_2O)]$ (A=Na and L=histidine)

$A_2[Zn(L)F_4(H_2O)].2H_2O$, (A=K and L=glutamic acid)

$A_2[Zn(L)F_4(H_2O)]$ (A=K and L=histidine)

Fig. 1. Proposed molecular structures of the complexes.

of 331–351°C, 483–503°C and 616–654°C (endothermic peaks at 453°C and 633°C) due to the loss of coordinated water molecule as well as decomposition of organic ligand. The relatively higher temperature required for removal of coordinated water probably be due to involvement of water molecule in hydrogen bonding interaction in the crystal lattice. Above 654°C, compound undergoes a continuous loss in weight as a consequence of which the final decomposition product could not be ascertained. Thermogram of $A_2[MnF_4(L)(H_2O)]$ (L = glutamic acid) showed that, the first stage of decomposition occurred between 114–161°C, corresponding to a loss of a water molecule (obsd. 4.14%; calcd. 4.8%). Above 170°C the compound undergo decomposition in gradual manner with the observed weight losses of 9.45%, 10.7% and 4.94% in the temperature ranges 170–223°C, 303–363°C and 481–966°C. The observed decomposition pattern attributed to fragmentation and thermal degradation of the organic moiety, however, decomposed fragments could not be estimated due to continuous weight loss in the process. DTA curve also corroborates the results by the presence of endothermic peaks at *ca.* 161°C, *ca.* 190°C and *ca.* 700°C respectively.

In case of, $A[MnF_4(L)(H_2O)]$ (L = proline) and $A[MnF_4(L)(H_2O)]$ (L = histidine) not much significant information could be obtained from the pyrolytic studies. Thermogram showed that the compound, $A[MnF_4(L)(H_2O)]$ (L = proline) starts losing weight at 443°C and this continues till 480°C (3.5%), followed by a horizontal till 569°C. Above 587°C a small loss in weight (1.71%) was also observed. TGA/DTA curve for $A[MnF_4(L)(H_2O)]$ (L = histidine,) exhibited a loss of weight, (7.13%) between 491–707°C, which may be ascribed to loss of a molecule of HF (calcd. 6.13%). However, above 707°C no appreciable change was observed in the thermogram.

Pyrolytic study involving fluoromanganate(II) complexes containing glutamic acid, aspartic acid and histidine exhibited similar behavior of fragmentation pattern with minor deviation, as observed in case of fluoromangante(III) complexes making any further discussion redundant (Supporting materials).

In case of fluoroglutamatozincate(II) complex, the thermogram exhibited first weight loss of 26.50% (calcd. 26.89%) corresponding to the loss of two molecules of lattice water

between 70–120°C. Further weight losses of 5.31% (calcd. 4.69%) and 38.80% (calcd. 40.02%) in the range of 250–290°C and 370–490°C are assignable to the loss of coordinated water molecule as well as fragmentation of organic ligand. The relatively higher temperature required for removal of coordinated water may be due to involvement of water molecule in hydrogen bonding interaction. Above 490°C compound undergoes continuous loss in weight. Thermogram of zincfluoro(histidine) complex exhibit almost continuous loss in weight as a result the fragmented moieties could not be ascertained with certainty. Thermogravimetric analysis provides good evidence in support of the molecular composition of the complexes.

Thus on the basis of chemical analyses in conjunction with spectral and thermogravimetric studies the probable molecular structures are proposed for the newly synthesized complexes (Fig. 1)

Conclusions

To conclude, it may be inferred that, a good number of fluoromanganate(III), fluoromanganate(II) and fluorozincate(II) complexes incorporating biogenic co-ligand amino acids have been synthesized from aqueous medium. The analytical data, results of thermogravimetric and spectral studies suggest that, the complexes possess octahedral or distorted octahedral structures. The room temperature magnetic moment measurements for the synthesized complexes exhibit values as expected for the presence of high spin d^4 manganese(III), d^5 manganese(II) and diamagnetic (d^{10}) zinc(II) ions in the synthesized complexes. The electronic spectral pattern suggests an appreciable splitting of ^5E_g ground state of manganese(III) ion in Mn(III) complexes. Thermogravimetric studies lend support to the molecular composition, also suggest a possibility of existence hydrogen bonding interactions in complexes reported herein. The simple aqueous medium based strategies for the synthesis of the complexes can serve as a paradigm for the synthesis of newer array of mixed-ligand fluoro complexes of other first row transition metal ions.

Acknowledgements

Supporting Information

IR and TGA data.

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