



REVIEW

Synthesis and Physico-Chemical Studies of Mixed-Ligand Fluoro Complexes of Some Transition Metals: A Review

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The chemistry of mixed ligand fluoro complexes of transition metals is an intriguing subject that has not yet been thoroughly investigated. Over the past three to four decades, there have been numerous reports of such complexes along with their synthesis, characterization, physico-chemical properties and in some cases crystallographic studies. This review summarizes the progress of some first row transition metal complexes consisting of fluoro as primary ligand and carboxylic, hydroxyl carboxylic, amino acids and nitrogen donor molecules such as pyridine, ethylene diamine, imidazole, 2,2'-bipyridine or 1,10-phenanthroline *etc.* as co-ligands with their synthesis, probable structures and physico-chemical properties.

Keywords: Mixed ligand fluoro complexes, Physico-chemical properties, Transition metals.

INTRODUCTION

The capability of fluoride ligands to stabilize anomalous oxidation states of transition metals is well recognized [1,2]. Being the most electronegative element, fluorine is able to produce an abundance of ionic ligands, which are characterized by their small size and extreme rigidity. The chemistry of transition metal fluoro complexes [3-13] is an intriguing area that still remains underexplored. Interesting aspects of mixed ligand fluoro complexes of transition metals include their peculiar reactivity [3,4], importance for activation metal mediated C-F binding [14] and effective catalysis [15]. Another reason for which mixed ligand fluoro compounds haven't gotten much attention is due to inadequate methods for integrating fluoro ligands. Since fluoride systems are known to etch glassware, chloro or bromo derivatives are normally used as starting materials for the production of mixed-ligand complexes since they are more accessible and easier to work with. The conversion of operations that are easily carried out with heavier halogens and hydrogen halides into F₂ and HF is significantly impeded by the difficulties that are associated with working with elemental fluorine and hydrogen fluoride [16]. Even though there is experimental equipment that can make dealing with F₂, HF

and MF_x easier, managing their reactivity is still difficult. Due to the strong hydrogen bonding, fluoride reagents hold water and other protic reagents with tenacity [17], making the preparation of pure fluoride reagents challenging [18,19]. As a result, the target fluoride may not be isolated, but rather, transition metal complexes comprising hydroxide [20] or bifluoride isolated. There are mixed-ligand fluoro compounds of transition metals reported in the literature [21], despite these many challenges. These include mixed-ligand fluoro complexes of transition metals containing carboxylic acid, hydroxy-carboxylic acid, biogenic co-ligands *viz.* glutamic acid, aspartic acid, histidine, proline, or cystine, neutral ligands like ethylene diamine, pyridine or imidazole, *etc.* as co-ligands. Mainly the mixed ligand fluoro complexes of manganese, copper, cobalt and zinc were studied. Earlier reviews focused mainly on the synthesis of organofluoride complexes of metals, and various types of properties [22-27]. During past three to four decades, there have been numerous reports on such complexes along with their synthesis, characterization, physico-chemical properties and in some cases crystallographic studies. Considering their unconventional synthetic procedure, special reactivity and diverse coordination ability of transition metals with various ligands, to the best of my knowledge, the syntheses, characterization, physico-

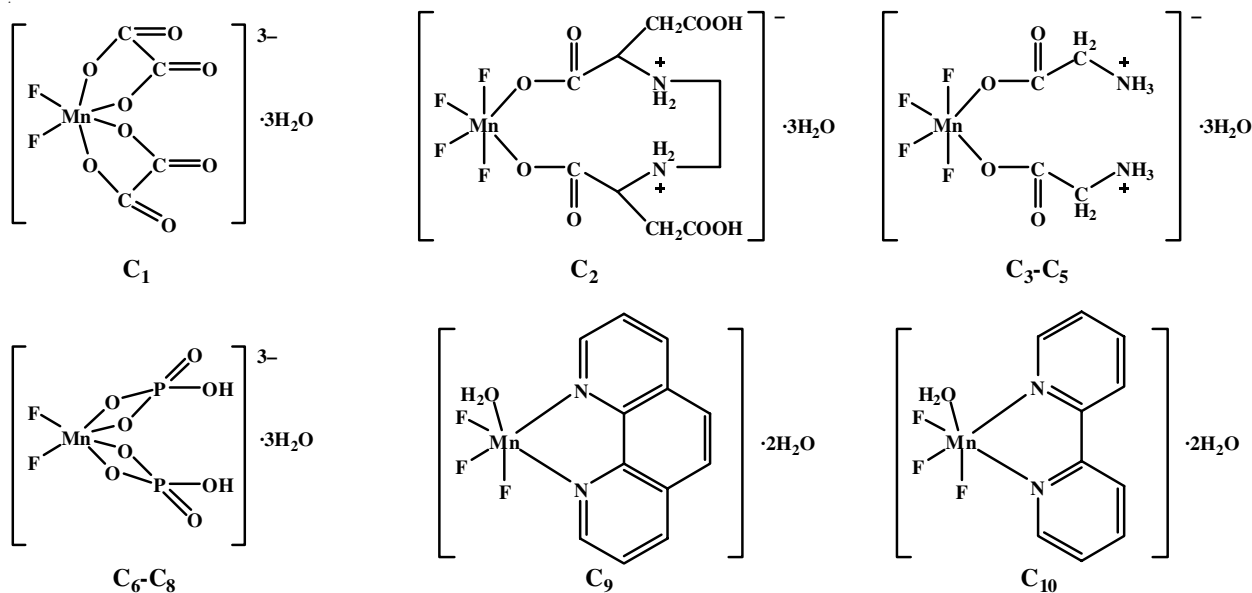
chemical properties of mixed ligand fluoro complexes of transition metals have not been reviewed yet.

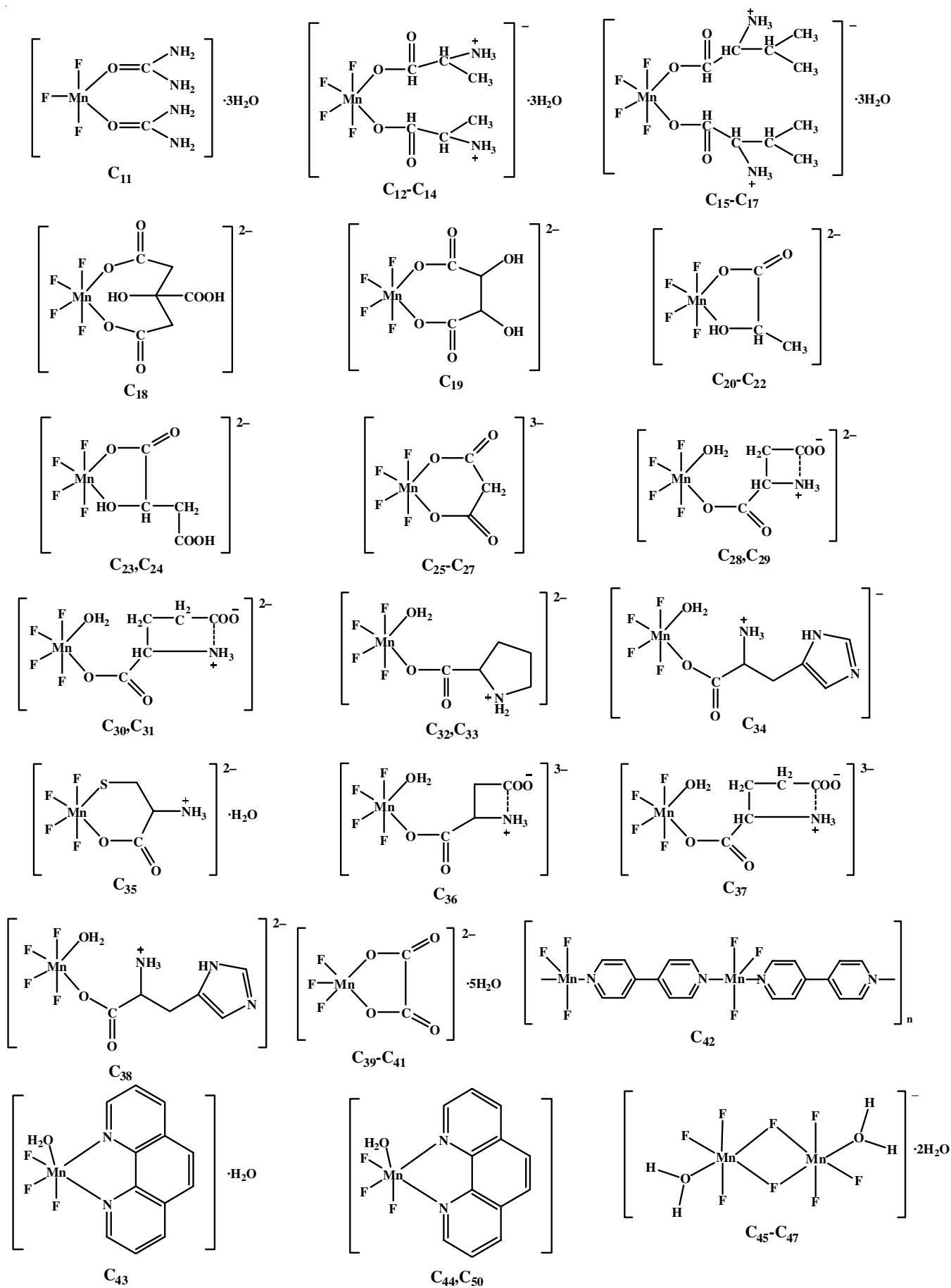
Synthesis and physico-chemical studies of mixed-ligand fluoro complexes of manganese: The versatility of manganese as a metal in numerous oxidation states makes it an indispensable cofactor for many redox enzymes [28-37]. Moreover, it is challenging to stabilize Mn(III) in aqueous medium [38], the tripositive state of manganese deserves special consideration due to its biochemical importance in various redox functions [28-37]. Stable manganese(III) building blocks have been proven to be a helpful precursor for single-molecule magnets [39,40] and it has been established that some manganese(III) complexes exhibit distinctive magnetic and structural properties [5,41-46]. Manganese(III) has the ability to undergo disproportionation in aqueous medium and has a fairly oxidizing power. These two characteristics make studying the coordination chemistry of manganese(III) challenging. Stable solid manganese(III) complexes are difficult to isolate for this reason. However, the formation of complexes is expected to lower the reduction potential of the Mn(III)/Mn(II) pair and thereby stabilize the Mn(III) [47]. Therefore, the determination of suitable ligands and sufficient techniques for the generation of stable Mn(III) complexes from aqueous solution is one of the most important prerequisites for future study. Fluoride, being a strong acidic ligand, significantly stabilizes Mn(III) both in solution and in solid form. Additionally, the coordination of fluoride generates anti-ferromagnetism in fluoromanganate(III) complexes [5,41-46]. The chemistry of mixed-ligand fluoromanganates(III) is anticipated to be significant and motivating since the inclusion of ligands alters the physico-chemical characteristics [48] in contrast to the corresponding binary complexes.

The distorted octahedral complex, $K_3[MnF_2(C_2O_4)_2] \cdot 3H_2O$ (**C**₁), was synthesized by the reaction of $H_2C_2O_4 \cdot 2H_2O$ and $KMnO_4$ in the presence of KF at *ca.* 0 °C. In this reaction, it is important to keep the fluoride concentration low in order to prevent the creation of $[MnF_3(C_2O_4)]^{2-}$ and $[MnF_3]^{2-}$. In the concentration ratio of Mn:EDTA:KF = 1:1:4, pink microcrystalline $K[MnF_4(EDTA)] \cdot 3H_2O$ (**C**₂) was produced by reacting $MnO(OH)$

in 40% HF with an EDTA solution containing minor amounts of KOH and KF. The mixed-ligand fluoromanganates(III), $Na[MnF_4(glyH)_2] \cdot 3H_2O$ (**C**₃), $K[MnF_4(glyH)_2] \cdot 3H_2O$ (**C**₄), $NH_4[MnF_4(glyH)_2] \cdot 3H_2O$ (**C**₅), $Na_3[MnF_2(HPO_4)_2] \cdot 3H_2O$ (**C**₆), $K_3[MnF_2(HPO_4)_2] \cdot 3H_2O$ (**C**₇), $(NH_4)_3[MnF_2(HPO_4)_2] \cdot 3H_2O$ (**C**₈), with HPO_4^{2-} and glycine (glyH), as coligands, were produced by reacting $MnO(OH)$ in 40% HF with their respective ligands in aqueous medium in the existence of alkali-metal fluoride (for HPO_4^{2-}) and alkali-metal carbonate (for glyH). Whereas the molecular mixed-ligand fluoro compounds, $[MnF_3(H_2O)(phen)] \cdot 2H_2O$ (**C**₉), $[MnF_3(H_2O)(bpy)] \cdot 2H_2O$ (**C**₁₀) and $[MnF_3(urea)_2] \cdot 3H_2O$ (**C**₁₁) (phen = 1,10-phenanthroline and bpy = 2,2'-bipyridine) were also synthesized by reacting $MnO(OH)$ in 40% HF with the corresponding ligand solutions. While **C**₁ decomposes relatively quickly, all of the other Mn(III) mixed-ligand fluoro complexes of are stable in the absence of moisture and may be stored for a considerable amount of time. The presence of Mn(III) in all the synthesized compounds assured from the chemically estimated oxidation state of the metal which was found to lie in the range 2.9-3.1. While the room temperature magnetic moment of compound **11** is 4.3 μ_B , the magnetic moments of other compounds varied from 4.78 to 5.0 μ_B . The pyrolysis of compound **11 ca.** 500 °C produces MnF_3 , a product that is highly esteemed for its potential as a fluorinating agent. The complexes produced probably have a distorted octahedral shape [49] (Fig. 1).

Purkayastha [50] also reported the mixed-ligand fluoromanganate(III) complexes of the type $Na[Mn(ala)_2F_4] \cdot 3H_2O$ (**C**₁₂), $K[Mn(ala)_2F_4] \cdot 3H_2O$ (**C**₁₃), $NH_4[Mn(ala)_2F_4] \cdot 3H_2O$ (**C**₁₄), $Na[Mn(val)_2F_4] \cdot 3H_2O$ (**C**₁₅), $K[Mn(val)_2F_4] \cdot 3H_2O$ (**C**₁₆) and $NH_4[Mn(val)_2F_4] \cdot 3H_2O$ (**C**₁₇) (ala = alanine and val = valine) containing amino acid as co-ligands. Complexes **C**₁₂-**C**₁₇ were prepared from the reaction of freshly prepared $MnO(OH)$ in 40% HF with the respective amino acids (alanine and valine) keeping Mn:F:amino acid ratio at 1:4:2. The magnetic moment values of complexes **15** and **16** were 4.6 and 4.7, while complexes **12** and **13** have values of 5.0 and 4.9, respectively. The slightly lower magnetic moment values in case of complex **15**





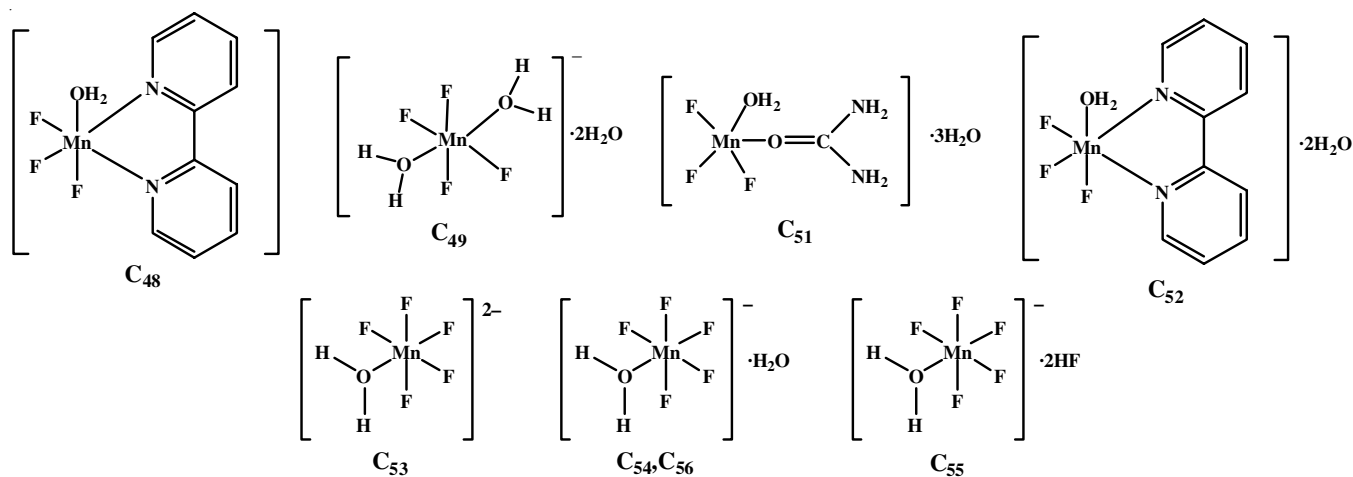


Fig. 1. Proposed molecular structures of the manganese complexes

and **17** indicate that there exists a possibility of weak antiferromagnetic interactions operating between continuous Mn(III) ions in the crystal lattice. The presence of two extra peaks in the FT-IR spectra at 3460 and 1635 cm^{-1} indicates that their forms and placements closely reflect those of the $\nu(\text{OH})$ and $\delta(\text{H-O-H})$ modes of lattice water, as shown in Table-1. A pyrolytic study of complex **17** clearly indicates the presence of an uncoordinated water molecule, as it loses one water molecule at 110 $^{\circ}\text{C}$ and then two molecules in between 150-160 $^{\circ}\text{C}$. The complexes **C**₁₂-**C**₁₇ are found to have a distorted octahedral structure (Fig. 1).

Bhowmik *et al.* [51] reported the mixed-ligand fluoromanganate(III) complexes, $\text{K}_2[\text{MnF}_4(\text{L})]$ (L = citric acid) (**C**₁₈), $\text{K}_2[\text{MnF}_4(\text{L})]$ (L = tartaric acid) (**C**₁₉) from aqueous medium.

The reported complexes were synthesized by reacting KMnO_4 , 40% HF with respective ancillary ligands (citric acid and tartaric acid) maintaining KMnO_4 :HF:ancillary ligand ratio as 1:4:1. The magnetic moment values of the complexes **18** and **19** to be 5.1 and 4.9 B.M., respectively. The electronic spectra of the complexes indicate significant splitting of the ${}^5\text{E}_g$ of Mn(III) ground state leading to a distorted octahedral structure (Table-2). The thermal studies of complex **18** indicate that the complex does not lose any mass upto 160 $^{\circ}\text{C}$, ruling out the possibility of lattice water in the complex and the complexes are presumed to have the following structure, according to chemical analyses and spectral studies (Fig. 1).

Bhowmik *et al.* [52] also synthesized mixed-ligand fluoromanganate(III) complex of the type $\text{Na}_2[\text{MnF}_4(\text{L})]$ (**C**₂₀) (L =

TABLE-1
SIGNIFICANT IR SPECTRAL (cm^{-1}) DATA OF THE MANGANESE COMPLEXES

Compd. No.	$\nu(\text{OH})$	$\nu_{\text{asy}}(\text{COO}^-)$	$\nu_{\text{sym}}(\text{COO}^-)$	$\delta_{\text{d}}(\text{NH}_3^+)/\delta(\text{H-O-H})$	$\delta_{\text{s}}(\text{NH}_3^+)$	$\nu(\text{Mn-F})$	$\nu(\text{Mn-O})$	$\nu(\text{Mn-N})$	Ref.
C ₁	3460	1680		1640		490			[49]
C ₂	3450	1723		1660		494		390	
C ₃ - C ₅	3445	1715		1640		505		355	
C ₁₁	3445	1535		1645		453			
C ₁₂ - C ₁₇	3460	1589	1410	1618	1531	480		412	[50]
C ₁₈	3419	1613	1410			415		353	[51]
C ₁₉	3417	1587	1350			446		393	
C ₂₀ - C ₂₂	3459-3464	1630-1658	1350-1380			583-585	485		[52]
C ₂₃ , C ₂₄	3430-3464	1600-1630	1394			610-615	480		
C ₂₅ - C ₂₇	3440	1630-1640	1350-1380			591-615	483-486		
C ₂₈ , C ₂₉	3421-3463	1501-1508	1310-1318	1619-1639	1423	567-590	475-478	450	[53]
C ₃₀ , C ₃₁	3463	1509	1354	1650-1655	1423	590	482	-	
C ₃₂ , C ₃₃		1639-1659	1385			483-497			
C ₃₄		1588	1344	1644	1411	499			
C ₃₅		1660	1384	1593	1450	467			
C ₃₆		1589	1355	1644	1421	551			
C ₃₇		1605	1364	1644	1429	553			
C ₃₈		1498	1336	1638	1414	631-530			
C ₃₉	3455	1670	1320	1640		495	425		[11]
C ₄₀	3460	1672	1365	1640		490	425		
C ₄₁		1670	1360			490	425		
C ₅₃	3460	1657	1486			584			[58]

TABLE-2
ELECTRONIC SPECTRAL DATA OF THE MANGANESE COMPLEXES

Compound No.	Compounds	ν_{\max} (cm ⁻¹)	Assignments	Ref.
C ₁	K ₃ [MnF ₂ (C ₂ O ₄) ₂].3H ₂ O	11,950	⁵ B _{1g} → ⁵ A _{1g}	[49]
		19,800	⁵ B _{1g} → ⁵ B _{2g}	
		22,220	⁵ B _{1g} → ⁵ E _g	
C ₂	K[MnF ₄ (EDTA)].3H ₂ O	11,800	⁵ B _{1g} → ⁵ A _{1g}	
		19,800	⁵ B _{1g} → ⁵ B _{2g}	
		22,220	⁵ B _{1g} → ⁵ E _g	
C ₃ -C ₅	Na[MnF ₄ (glyH) ₂].3H ₂ O	12,000	⁵ B _{1g} → ⁵ A _{1g}	
	K[MnF ₄ (glyH) ₂].3H ₂ O	19,800	⁵ B _{1g} → ⁵ B _{2g}	
	NH ₄ [MnF ₄ (glyH) ₂].3H ₂ O	21,300	⁵ B _{1g} → ⁵ E _g	
C ₆ -C ₈	Na ₃ [MnF ₂ (HPO ₄) ₂].3H ₂ O	11,000	⁵ B _{1g} → ⁵ A _{1g}	
	K ₃ [MnF ₂ (HPO ₄) ₂].3H ₂ O	18,200	⁵ B _{1g} → ⁵ B _{2g}	
	(NH ₄) ₃ [MnF ₂ (HPO ₄) ₂].3H ₂ O	20,800	⁵ B _{1g} → ⁵ E _g	
C ₉	[MnF ₃ (H ₂ O)(phen)].2H ₂ O	13,750	⁵ B _{1g} → ⁵ A _{1g}	
		19,000	⁵ B _{1g} → ⁵ B _{2g}	
		23,250	⁵ B _{1g} → ⁵ E _g	
C ₁₀	[MnF ₃ (H ₂ O)(bpy)].2H ₂ O	13,750	⁵ B _{1g} → ⁵ A _{1g}	
		19,000	⁵ B _{1g} → ⁵ B _{2g}	
		23,250	⁵ B _{1g} → ⁵ E _g	
C ₁₁	[MnF ₃ (urea) ₂].3H ₂ O	10,810	⁵ B _{1g} → ⁵ A _{1g}	
		17,240	⁵ B _{1g} → ⁵ B _{2g}	
		20,620	⁵ B _{1g} → ⁵ E _g	
C ₁₂ -C ₁₄	Na[Mn(ala) ₂ F ₄].3H ₂ O	13,831	⁵ B _{1g} → ⁵ A _{1g}	[50]
	K[Mn(ala) ₂ F ₄].3H ₂ O	19,436	⁵ B _{1g} → ⁵ B _{2g}	
	NH ₄ [Mn(ala) ₂ F ₄].3H ₂ O	24,906	⁵ B _{1g} → ⁵ E _g	
C ₁₅ -C ₁₇	Na[Mn(val) ₂ F ₄].3H ₂ O	14,705	⁵ B _{1g} → ⁵ A _{1g}	
	K[Mn(val) ₂ F ₄].3H ₂ O	21,739	⁵ B _{1g} → ⁵ B _{2g}	
	NH ₄ [Mn(val) ₂ F ₄].3H ₂ O	24,154	⁵ B _{1g} → ⁵ E _g	
C ₁₈ , C ₁₉	K ₂ [MnF ₄ (L)] (L = citric acid)	–	–	[51]
	K ₂ [MnF ₄ (L)] (L = tartaric acid)	18,240-20,000 21,990-22,220	⁵ B _{1g} → ⁵ B _{2g} ⁵ B _{1g} → ⁵ E _g	
C ₂₀ -C ₂₂	Na ₂ [MnF ₄ (L)] (L = lactate),	11,950	⁵ B _{1g} → ⁵ A _{1g}	[52]
	K ₂ [MnF ₄ (L)] (L = lactate),	18,348	⁵ B _{1g} → ⁵ B _{2g}	
	(NH ₄) ₂ [MnF ₄ (L)] (L = lactate)	23,866	⁵ B _{1g} → ⁵ E _g	
C ₂₃ , C ₂₄	Na ₂ [MnF ₄ (L)] (L = malate)	12,280	⁵ B _{1g} → ⁵ A _{1g}	
	K ₂ [MnF ₄ (L)] (L = malate)	19,120	⁵ B _{1g} → ⁵ B _{2g}	
		23,250	⁵ B _{1g} → ⁵ E _g	
C ₂₅ -C ₂₇	Na ₃ [MnF ₄ (L)].H ₂ O	12,500	⁵ B _{1g} → ⁵ A _{1g}	
	K ₃ [MnF ₄ (L)].H ₂ O	18,181	⁵ B _{1g} → ⁵ B _{2g}	
	(NH ₄) ₃ [MnF ₄ (L)].H ₂ O (L = malonate)	–	–	
C ₂₈ , C ₂₉	Na ₂ [MnF ₄ (L)H ₂ O]	14,700	⁵ B _{1g} → ⁵ A _{1g}	[53]
	(NH ₄) ₂ [MnF ₄ (L)H ₂ O] (L = aspartic acid)	19,200	⁵ B _{1g} → ⁵ B _{2g}	
		25,000	⁵ B _{1g} → ⁵ E _g	
C ₃₀ , C ₃₁	Na ₂ [MnF ₄ (L)H ₂ O]	–	–	
	K ₂ [MnF ₄ (L)H ₂ O] (L = glutamic acid)	19,200	⁵ B _{1g} → ⁵ B _{2g}	
		25,000	⁵ B _{1g} → ⁵ E _g	
C ₃₂ , C ₃₃	Na ₂ [MnF ₄ (L)(H ₂ O)]	15,800	⁵ B _{1g} → ⁵ A _{1g}	
	K ₂ [MnF ₄ (L)(H ₂ O)] (L = proline)	22,200	⁵ B _{1g} → ⁵ B _{2g}	
C ₄₀	K ₂ [MnF ₃ (C ₂ O ₄)].H ₂ O (C ₂ O ₄ ²⁻ = oxalato)	–	–	[11]
		19,800	⁵ B _{1g} → ⁵ B _{2g}	
		22,700	⁵ B _{1g} → ⁵ E _g	
C ₄₁	(NH ₄) ₂ [MnF ₃ (C ₂ O ₄)] (C ₂ O ₄ ²⁻ = oxalato)	–	–	
		19,500	⁵ B _{1g} → ⁵ B _{2g}	
		22,500	⁵ B _{1g} → ⁵ E _g	
C ₄₃	[Mn(phen)F ₃ (H ₂ O)].H ₂ O	14,500	⁵ B _{1g} → ⁵ A _{1g}	[55]
		18,300	⁵ B _{1g} → ⁵ B _{2g}	
		21,900	⁵ B _{1g} → ⁵ E _g	

lactate), $K_2[MnF_4(L)]$ (C_{21}) ($L = \text{lactate}$), $(NH_4)_2[MnF_4(L)]$ (C_{22}) ($L = \text{lactate}$), $Na_2[MnF_4(L)]$ ($L = \text{malate}$) (C_{23}), $K_2[MnF_4(L)]$ ($L = \text{malate}$) (C_{24}), $Na_3[MnF_4(L)] \cdot H_2O$ ($L = \text{malonate}$) (C_{25}), $K_3[MnF_4(L)] \cdot H_2O$ ($L = \text{malonate}$) (C_{26}) and $(NH_4)_3[MnF_4(L)] \cdot H_2O$ ($L = \text{malonate}$) (C_{27}), by reacting $MnO(OH)$, 40% HF with the respective hydroxy acids in presence of alkali metal carbonate. The observed values of the magnetic moment and the electronic spectral positions (Table-2) clearly indicate that all the synthesized complexes (C_{20} - C_{27}) contains high spin Mn(III) ion. The frequency difference between the two modes, $\Delta\nu [v_{\text{asy}}(\text{COO})-v_{\text{sym}}(\text{COO})]$, greater than 200 cm^{-1} suggests that the mode of coordination of COO^- group to the metal center in an unidentate fashion [21]. Complexes C_{23} and C_{24} also show an absorption band at *ca.* 1710 cm^{-1} is attributable to $\nu(\text{COOH})$ and suggests the presence of an undissociated terminal carboxylic group which is not coordinated. Electrochemical study of complex C_{25} shows a quasi-reversible behaviour attributable to Mn(III)/Mn(II) pair based on the observed E_0 and E_p values of 1.0 V and 2.11 V, respectively when scanned at a rate of 0.2 V s^{-1} whereas complex C_{27} has one irreversible reduction peak at +0.6 V without any anodic peak. According to the scanning electron microscopy (SEM) results, the surface layers of malate complexes are homogenous, whereas the surface layers of lactate and malonate complexes are partially homogeneous.

In continuation of their work, Bhowmik *et al.* [53] also synthesized mixed-ligand fluoromanganate(III) of type $Na_2[MnF_4(L)H_2O]$ ($L = \text{aspartic acid}$) (C_{28}), $(NH_4)_2[MnF_4(L)H_2O]$ ($L = \text{aspartic acid}$) (C_{29}), $Na_2[MnF_4(L)H_2O]$ ($L = \text{glutamic acid}$) (C_{30}), $K_2[MnF_4(L)H_2O]$ ($L = \text{glutamic acid}$) (C_{31}), $Na_2[MnF_4(L)(H_2O)]$ ($L = \text{proline}$) (C_{32}), $K_2[MnF_4(L)(H_2O)]$ ($L = \text{proline}$) (C_{33}), $Na[MnF_4(L)(H_2O)]$ ($L = \text{histidine}$) (C_{34}), $Na_2[MnF_4(L)] \cdot H_2O$ ($L = \text{cysteine}$) (C_{35}), $K_3[Mn(L)F_4]$ ($L = \text{aspartic acid}$) (C_{36}), $K_3[Mn(L)F_4]$ ($L = \text{glutamic acid}$) (C_{37}) and $K_3[Mn(L)F_4]$ ($L = \text{histidine}$) (C_{38}). Syntheses of host of mixed-ligand fluoro complexes of Mn(II) and Mn(III) with amino acids as biogenic co-ligands *viz.* aspartic acid, proline, glutamic acid, cysteine and histidine, were synthesized by reacting $MnO(OH)/Mn(OH)_2$ in 40%HF and the corresponding amino acids in a ratio of 1:4:1 at pH ~3-6, with an A_2CO_3 or AOH solution ($A = \text{Na, K, NH}_4$). According to the physico-analytical data, thermogravimetric and spectral studies, the complexes have octahedral or distorted octahedral structures (Fig. 1). The results of magnetic moment measurements at room temperature for the synthesized complexes show values which are typical for the existence of high spin d^4 manganese(III) and d^5 manganese(II) ions system. The UV-visible spectroscopic studies of the Mn(III) complexes indicate significant splitting of the 5E_g of manganese(III) ground state.

Bhattacharjee *et al.* [11] reported the synthesis of mixed-ligand fluoromanganate(III) complexes, $Na_2[MnF_3(C_2O_4)] \cdot 5H_2O$ (C_{39}), $K_2[MnF_3(C_2O_4)] \cdot H_2O$ (C_{40}) and $(NH_4)_2[MnF_3(C_2O_4)]$ ($C_2O_4^{2-} = \text{oxalato}$) (C_{41}). The complexes were synthesized by reacting $MnO(OH)$ in 40% HF and $A_2C_2O_4$ ($A = \text{Na, K, NH}_4$) in a ratio of 1/4-5/1 at $0-20^\circ\text{C}$ resulted a pink coloured solution, which was then used to isolate the dark pink microcrystalline compounds C_{39} , C_{40} and C_{41} by adding ethanol. The magnetic moments of the compounds at room temperature, lying in the

range 4.2-4.3 μ_B , indicate the probability of a solid state polymeric structure of $[MnF_3(C_2O_4)]^{2-}$ *via* the -Mn-F-Mn- linkage or involving both F and $C_2O_4^{2-}$ as bridging groups that enable the functioning of a weak antiferromagnetic interaction between neighboring Mn^{3+} ions. The electronic spectra of complex C_{40} and C_{41} were recorded using a solution that contains a minor amount of 40% HF. The transitions ${}^5B_{1g} \rightarrow {}^5B_{2g}$ and ${}^5B_{1g} \rightarrow {}^5E_g$ in the UV-visible spectra of the complexes C_{39} - C_{41} observed at *ca.* 19600 and *ca.* 22600 cm^{-1} , respectively (Table-2). This indicates significant splitting of the 5E_g of Mn^{3+} ground state in $[MnF_3(C_2O_4)]^{2-}$ as a result of Jahn-Teller effects. The FT-IR spectra of the complexes are comparable and exhibit prominent absorptions for the coordinated $C_2O_4^{2-}$ and F^- groups. Appearance of band at *ca.* 495-490 cm^{-1} are assignable to $\nu(\text{Mn-F})$ (Table-1) modes of coordinated fluoride. The presence of a bridging oxalato group is confirmed by the existence of absorptions due to the $C_2O_4^{2-}$ group. The absence of a 1750-1680 cm^{-1} band suggests a chelated oxalato ligand in the complexes.

Darriet *et al.* [54] also successfully synthesized 4,4'-bipyMnF₃ (C_{42}) by using $Mn^{III}/4,4'$ -bipy/HF/ H_2O /methanol/acetone system. The crystalline structure of this compound was determined by single crystal X-ray diffraction at different temperatures and it was found that Mn^{III} is octahedrally coordinated with four fluoride and two nitrogen ligands.

Biju & Rajasekharan [55] reported the synthesis and crystal structure of $[Mn(\text{phen})F_3(H_2O)] \cdot H_2O$ (C_{43}) and $Mn(\text{phen})F_3(H_2O)$ (C_{44}) in the anhydrous form. Although both were formed from the same procedure, but the crystal structures of C_{43} and C_{44} can be differentiated themselves. DFT calculations were carried out to verify its applicability for assigning the electronic transition energies of this d^4 system. Intermolecular hydrogen interactions between coordinated fluoride ions and water molecules affect Mn-F distances. The presence of a static Jahn-Teller effect causes a reduction in the lengths of the axial bonds, which in turn indirectly affects these bond lengths. The hypotheses obtained from density functional theory are compared to the assignments of the electronic spectral bands. The transition with the lowest energy exhibits a significant difference with the calculation of an isolated molecule, but transitions with higher energy levels display a robust agreement with the calculation. As the molecular configuration of Mn(III) complex is almost identical in both crystals, channels are formed in the hydrate which are occupied with water molecules.

Rother *et al.* [56] also synthesized another type of mixed ligand fluoromanganate(III) complexes *viz.* $\text{dabcoH}_2[Mn_2F_8(H_2O)_2] \cdot 2H_2O$ (C_{45}), $\text{pipzH}_2[Mn_2F_8(H_2O)_2] \cdot 2H_2O$ (C_{46}) and $(\text{dabcoH}_2)_2[Mn_2F_8(H_2PO_4)_2]$ (C_{47}) using biprotonated dabco (1,4-diazabicyclo[2.2.2]octane) or pipz (piperazine) as counter cations. The dimeric anions formed by $[Mn_2F_8O]$ octahedra (O from oxoligands) that share an edge and display highly asymmetric double fluorine bridges are observed in each of the three compounds. The enormous elongation of the octahedral axis, which includes the long bridging Mn-F and Mn-O bonds, is a clear indication of the strong pseudo-Jahn-Teller effect that occurs in the octahedral manganese(III) complexes. The octahedral geometry is almost identical to that of the aqua-fluoro compounds, even though the anion charge is different in fluoride

phosphate. On the other hand, the ligand field spectra also show the strong distortion.

Pedro-Núñez *et al.* [57] reported the synthesis of $[\text{MnF}_3(\text{H}_2\text{O})(2,2'\text{-bipy})]$ (C_{48}) and $4,4'\text{-bipyH}_2[\text{MnF}_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (C_{49}), where bipy = bipyridyl group. The octahedral manganese geometry in both complexes significantly distorted by the Jahn-Teller effect due to the high-spin d^4 configuration of Mn^{3+} . Both compounds include a very extensive intermolecular structure of hydrogen bonding. These findings are compared to other existing fluoro compounds of Mn(III). However, there are additional similar complexes that have been synthesized for example $[\text{MnF}_3(\text{H}_2\text{O})(\text{phen})]$ (C_{50}), $[\text{MnF}_3(\text{H}_2\text{O})\{\text{NH}_2\text{-C(O)NH}_2\}] \cdot 3\text{H}_2\text{O}$ (C_{51}) and $[\text{MnF}_3(\text{H}_2\text{O})\text{B}] \cdot 2\text{H}_2\text{O}$, (C_{52}) [where B = 2,2'-bipy or 1,10-phenanthroline (phen)].

The crystal structure and synthesis of another type of novel fluoromanganate(III), $[(\text{H}_3\text{N}(\text{CH}_2)_2)_2\text{NH}_2]_2[\text{MnF}_5(\text{H}_2\text{O})_3]$ (C_{53}) was also reported by Pedro-Núñez and co-workers [58]. Due to the Jahn-Teller effect, $[\text{MnF}_5(\text{H}_2\text{O})]^{2-}$ anions to be octahedral with a strong distortion along the F-Mn-OH₂ axes. A chain of octahedra connected by double-hydrogen bonds is affirmed by the existence of a rich structure of intermolecular hydrogen bond. The intraconfigurational d^4 transitions split by a ligand field of C_{4v} symmetry is used to explain polarized optical spectra on the single crystals. Based on this work, Rother *et al.* [59] further reported the synthesis and structural details of three additional aqua-pentafluoromanganate(III) complexes, $\text{NMpipzH}_2[\text{MnF}_5(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (C_{54}) (NMpipz = N-Methyl piperazine), $N,N'\text{-DMpipzH}_2[\text{MnF}_5(\text{H}_2\text{O})] \cdot 2\text{HF}$ (C_{55}) ($N,N'\text{-Dmpipz}$ = N,N' -dimethyl piperazine) and $N,N\text{-DMenH}_2[\text{MnF}_5(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (C_{56}) ($N,N\text{-DmenH}_2$ = N,N -dimethylethylenediamine).

Synthesis and physico-chemical studies of mixed-ligand fluoro complexes of copper: Information regarding mixed-ligand fluorocuprates(II) are limited in the literature [60,61]. Such kind of transition metal complexes makes it possible to compare their characteristics to those of corresponding binary fluoro complexes. Furthermore, mixed-fluoro copper complexes exhibit a number of interesting characteristics [5,7,8,62-64], some of which also have biochemical significance [61,65].

Bhattacharjee & Choudhury [66] reported the synthesis of $(\text{H}_2\text{Im})_4[\text{CuF}_6]$ (C_{57}) by reacting $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with ammonium bifluoride (NH_4HF_2) and imidazole at pH 6-7. The interactions between $\text{CuO} \cdot n\text{H}_2\text{O}$ with 40% HF in the presence of

imidazole were used to obtain $(\text{H}_2\text{Im})_2[\text{CuF}_4(\text{H}_2\text{O})_2]$ (C_{58}), (H_2Im = imidazolium cation). The magnetic moment evaluated for complexes **57** and **58** was found to be 1.86 B.M. and 1.88 B.M., respectively in line with mononuclear copper(II) (d^9) system. The relatively low value for the fluoro complexes may be due to a Cu-F...Cu-F interaction in the solid state.

Bhattacharjee & Choudhury [67] also reported the synthesis of the copper complexes of the type $(\text{H}_2\text{gly})_4[\text{CuF}_6]$ (C_{59}), $\text{NH}_4[\text{CuF}_3(\text{Hgly})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (C_{60}) and $\text{NH}_4[\text{CuF}_3(\text{L-ala})(\text{H}_2\text{O})_2]$ (C_{61}), by reacting hydrated copper(II) oxide with amino acids in the presence of bifluoride $[\text{HF}_2^-]$ in the aqueous medium. Synthesis is sensitive to the sequence in which ligands, fluoride and amino acids were added. It appears that mixed-ligand fluoro complexes seem to be more easily formed in reaction solutions with pH values lower than the isoelectronic points of the respective amino acids. The amino acids, which exist as zwitterions was found to be an unexpected non-chelated kind of co-ligand in the complexes were shown to be bound to the copper(II) centre *via* the carboxyl ($-\text{COO}^-$) group. A copper(II) complex with six coordinates is compatible with the ESR and magnetic moment measurements (Fig. 2).

Bhattacharjee *et al.* [68] also reported that the synthesis of $\text{Na}[\text{CuF}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ (C_{62}), $\text{K}[\text{CuF}(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ (C_{63}) and $\text{NH}_4[\text{CuF}(\text{SO}_4)] \cdot 3\text{H}_2\text{O}$ (C_{64}). In these complexes, distorted octahedral polymeric structure was formed with F^- and SO_4^- as bridge ligands, which indicates the presence of the $[\text{CuF}(\text{SO}_4)]^-$ species.

Synthesis and physico-chemical studies of mixed-ligand fluoro complexes of zinc: Although ternary zinc complexes with various anions Cl^- , Br^- , SCN^- , NO_3^- , *etc.* as ancillary ligands have been extensively studied, but fluoride as co-ligands are rare. Reports on the mixed-ligand complexes of zinc(II) containing fluoride are also limited, however, some of the them are discussed below,

Bhowmik *et al.* [53] also synthesized the mixed-ligand fluorozincate(II) complexes of type $\text{K}_2[\text{Zn}(\text{L})\text{F}_4(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (L = glutamic acid) (C_{65}) and $\text{K}_2[\text{Zn}(\text{L})\text{F}_4(\text{H}_2\text{O})]$ (L = histidine), (C_{66}) by reacting freshly prepared $\text{Zn}(\text{OH})_2$, 40% HF and the respective co-ligands in a ratio of 1:4:1 at pH *ca.* 6.5 in presence of 2 N KOH solution. The complexes were precipitated by adding pre-cooled ethanol solvent. The compounds exhibit monodentate coordination of the amino acid's carboxylate

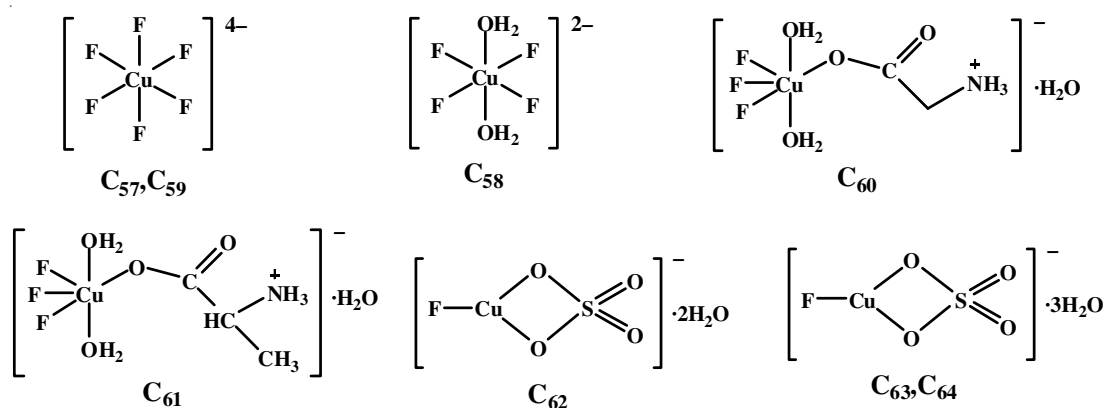


Fig. 2. Proposed molecular structures of the copper complexes

group as the frequency difference between $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ ($\Delta\nu$) is more than 200 cm^{-1} (Fig. 3). Furthermore, the complex shows a strong band at $\sim 1730\text{ cm}^{-1}$ can be attributed to the presence of a carboxylic (COOH) group in the compound which is non-ionized.

Goswami *et al.* [69] also reported the ternary fluoro complex of zinc(II), $[\text{ZnF}_2(\text{Bim})(\text{H}_2\text{O})]$ (C_{67}) (Bim = benzimidazole) was synthesized from a reaction procedure where hydrated metal(II) oxide and benzimidazole were mixed with bifluoride in aqueous medium at pH 6. The complex exhibited fluorescence at 370 nm upon excitation at 271 nm.

Synthesis and physico-chemical studies of mixed-ligand fluoro complexes of cobalt: The literature on the mixed-ligand fluorocobaltates (II) is also sparse. Divalent cobalt forms complexes of several stereochemical kinds [70] with a range of N-donor ligands, ranging from monodentate to multi-dentate macrocyclic and this area of cobalt(II) chemistry is still actively studied. In addition, there have been reports of hetero-ligand N-donor halo complexes of cobalt(II) [71-73].

Bhattacharjee *et al.* [63] synthesized three mixed-ligand fluorocobaltate(II) complexes *viz.* $\text{Na}[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$ (C_{68}), $\text{K}[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$ (C_{69}) and $\text{NH}_4[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$ (C_{70}). The synthesis was carried out at steam-bath temperature using a 1:2:1 ratio of $\text{Co}(\text{OH})_2$ to AF and A_2SO_4 , (A = NH_4 , Na or K) in the presence of little quantity of 40% HF. The magnetic moments and electronic spectra of $[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]^-$ suggest an octahedral or a distorted octahedral structure for cobalt(II). The occurrence of a bridging bidentate sulphate ligand is revealed by IR and laser Raman spectral studies.

Four novel mixed-ligand fluorocobaltate(II) complexes containing N-donor co-ligands *viz.* $[\text{Co}(\text{N}_2\text{H}_4)_2\text{F}_2] \cdot 2\text{H}_2\text{O}$ (C_{71}), $[\text{Co}(\text{dmpz})\text{F}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (C_{72}), $[\text{phenH}][\text{CoF}_3(\text{phen})] \cdot 8\text{H}_2\text{O}$ (C_{73}) and $[\text{bipyH}][\text{CoF}_3(\text{bipy})] \cdot 6\text{H}_2\text{O}$ (C_{74}) (dmpz = 3,5-dimethylpyrazole, phen = 1,10-phenanthroline and bipy = 2,2'-bipyridine) were synthesized by reacting $\text{Co}(\text{OH})_2$ in 40% HF containing hydrazine at pH < 5 [74]. In order to obtain $\text{Co}^{\text{II}}\text{-dmpz-F}$ complex with contemporary ligand 3,5-dimethylpyrazole (dmpz) on a cobalt(II) centre from the reaction of $\text{Co}(\text{acac})_2$, F^- and N_2H_4 or $\text{Co}(\text{N}_2\text{H}_4)_2\text{F}_2$, F^- and acacH (acacH = acetylacetonate) generate in the form of $[\text{Co}(\text{dmpz})\text{F}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{dmpz}')_2$ (dmpz' = dmpz-H), respectively, demonstrated that the ligand has formed on the metal. The complex ion in all cases exhibit a distorted octahedral structure (Fig. 3), but $[\text{Co}(\text{N}_2\text{H}_4)_2\text{F}_2]$ is discrete and in other cases it is polymeric containing F^- as a bridging ligand.

Conclusion

In conclusion, the first-row transition metal mixed-ligand fluoro complexes of manganese, copper, cobalt and zinc containing carboxylic, hydroxyl carboxylic, amino acids and nitrogen donor such as pyridine, ethylene diamine, imidazole, 2,2'-bipyridine or 1,10-phenanthroline, *etc.* as co-ligands were discussed in detail. All the mixed ligand complexes probably have an octahedral or distorted octahedral structure and have normal magnetic moments. This review will help to provide a base information to the scientific community about the scope in the chemistry of the mixed-ligand fluoro complexes of transition metals and to extend these studies to other coordination fluoro complexes system.

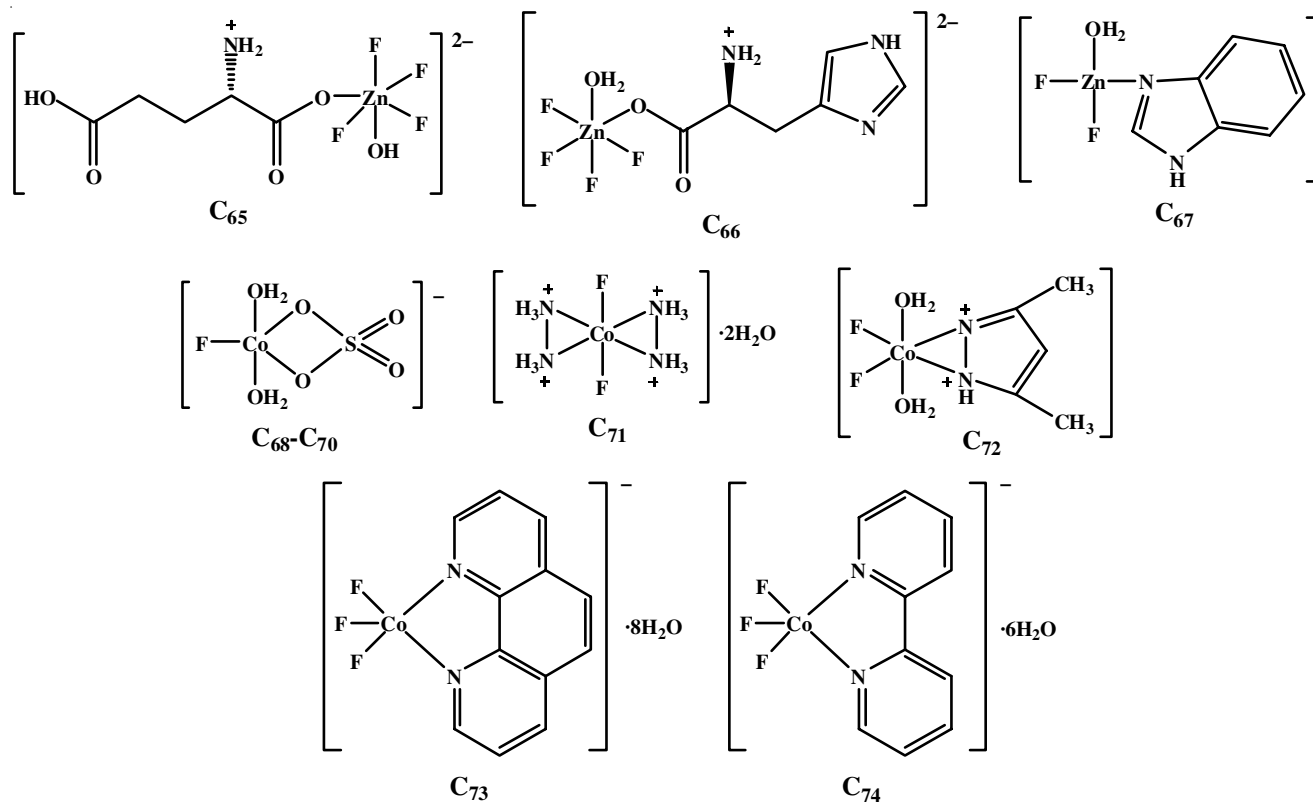


Fig. 3. Proposed molecular structures of the zinc and cobalt complexes

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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