

STUDIES ON  
FLUORO, MIXED-FLUORO, AND ACETYLACETONATO COMPLEXES OF  
COBALT(II) AND COPPER(II)  
AND  
PEROXO-COMPLEXES OF COPPER(II)

***MINAKSHI DEVI***

DEPARTMENT OF CHEMISTRY  
SCHOOL OF PHYSICAL SCIENCES  
NEHU

A THESIS  
SUBMITTED  
IN  
FULFILMENT OF THE REQUIREMENT OF THE DEGREE OF  
**DOCTOR OF PHILOSOPHY**



To



**THE NORTH-EASTERN HILL UNIVERSITY  
SHILLONG  
INDIA**

**JUNE, 1988**

STUDIES ON  
MORALE, MOTIVATION, AND ATTITUDE  
IN THE  
INDUSTRIAL AND  
BUSINESS SITUATION

ABSTRACT

The results of investigations related to morale, motivation and application of personnel in industry and business are presented in this book. The book is divided into six chapters. The first chapter is a general introduction and the following chapters are:

# ABSTRACT

Chapter I, provides a brief introduction to the book, which is divided into six chapters. The first chapter is a general introduction and the following chapters are:

Chapter II, provides a brief introduction to the book, which is divided into six chapters. The first chapter is a general introduction and the following chapters are:

Chapter III, provides a brief introduction to the book, which is divided into six chapters. The first chapter is a general introduction and the following chapters are:

Chapter IV, provides a brief introduction to the book, which is divided into six chapters. The first chapter is a general introduction and the following chapters are:

Chapter V, provides a brief introduction to the book, which is divided into six chapters. The first chapter is a general introduction and the following chapters are:

Chapter VI, provides a brief introduction to the book, which is divided into six chapters. The first chapter is a general introduction and the following chapters are:

---

STUDIES ON  
FLUORO, MIXED-FLUORO, AND ACETYLACETONATO  
COMPLEXES OF COBALT(II) AND COPPER(II)  
AND  
PEROXO-COMPLEXES OF COPPER(II)

---

ABSTRACT

The results of investigations related to fluoro, mixed-fluoro and acetylacetonato complexes of cobalt(II) and copper(II), as well as those related to peroxo-copper(II) complexes form the basis of the present thesis. The new results have been prefaced with a brief general introduction and the contents of the thesis have been distributed over six Chapters.

Chapter 1 presents a brief introduction pertaining to the work embodied in the thesis. The importance of and the interest in the studies of fluoro and mixed-fluoro compounds of metals, in general, and those of cobalt(II) and copper(II), in particular, have been highlighted. The problems encountered in the reported methods of synthesis of acetylacetonato compounds of cobalt(II) and copper(II) are also emphasised therein.

Apart from this, attention has also been drawn to the significance and contemporary interest in the study of peroxo-transition metal compounds, especially peroxo-copper(II)

complexes. This Chapter also projects the scope of work on the chosen aspects of cobalt and copper chemistry.

Chapter 2 gives the details of the methods of elemental analyses and the instruments/equipment used for characterisation and structural assessment of the newly synthesised compounds.

Chapter 3 of the thesis deals with a direct synthesis of alkali trifluorocobaltate(II) monohydrates,  $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$  ( $A = \text{Na}, \text{K}$  or  $\text{NH}_4$ ), and the first synthesis and structural assessment of mixed-ligand fluoro-complexes of cobalt(II),  $[\text{Co}(\text{NH}_3)_4\text{F}_2]$ ,  $A[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$  ( $A = \text{Na}, \text{K}$  or  $\text{NH}_4$ ),  $[\text{CoF}_2(\text{N}_2\text{H}_4)_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Co}(\text{dmpz})\text{F}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (dmpz=3,5-dimethylpyrazole,  $\text{C}_5\text{H}_8\text{N}_2$ ) and  $[\text{LH}][\text{CoF}_3\text{L}] \cdot n\text{H}_2\text{O}$  ( $L = 1,10$ -phenanthroline(phen) $n=8$ ;  $L = 2,2'$ -bipyridine(bipy) $n=6$ ).

Syntheses of the complexes were accomplished by the following methods:

- i) The pink microcrystalline  $A[\text{CoF}_3] \cdot \text{H}_2\text{O}$  ( $A = \text{Na}, \text{K}$ , or  $\text{NH}_4$ ) have been synthesised from the reaction of  $\text{Co}(\text{OH})_2$  with  $\text{AF}$  in 40%  $\text{HF}$  at  $\text{pH} < 3$  followed by precipitation with ethanol. While a higher  $\text{pH}$  (5-6), maintained by the addition of  $\text{AOH}$ , contaminates the product for  $A = \text{Na}$  or  $\text{K}$ , a molecular complex  $[\text{Co}(\text{NH}_3)_4\text{F}_2]$  is formed in the case where aqueous ammonia is used to raise the  $\text{pH}$ .
- ii) The synthesis of mixed-fluorocobaltates(II) of the type  $A[\text{CoF}(\text{SO}_4)(\text{H}_2\text{O})_2]$  ( $A = \text{Na}, \text{K}$  or  $\text{NH}_4$ ) has been achieved from the reaction of  $\text{Co}(\text{OH})_2$  with  $\text{AF}$  and  $\text{A}_2\text{SO}_4$ , in the ratio of 1:2:1, in the presence of

a very small amount of 40% HF at a steam-bath temperature.

- iii) Difluorobis(hydrazine)cobalt(II) dihydrate,  $[\text{CoF}_2(\text{N}_2\text{H}_4)_2] \cdot 2\text{H}_2\text{O}$ , and diaqua(3,5-dimethylpyrazole) difluorocobalt(II) dihydrate,  $[\text{Co}(\text{dmpz})\text{F}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , were prepared from the reaction of  $\text{Co}(\text{OH})_2$  with a minimum amount of 40% HF, and hydrazine hydrate and an ethanolic solution of 3,5-dimethylpyrazole, respectively, in the ratio of  $\text{Co}:\text{L}(\text{L}=\text{N}_2\text{H}_4 \text{ or } \text{dmpz})$  as 1:2. The syntheses were carried out in an ice-cold condition.
- iv)  $[\text{LH}][\text{CoF}_3\text{L}] \cdot n\text{H}_2\text{O}$  ( $\text{L}=\text{phen}$ ,  $n=8$ ;  $\text{L}=\text{bipy}$ ,  $n=6$ ) was synthesised from the reaction of  $\text{Co}(\text{OH})_2$  with a minimum amount of 40% HF and ethanolic solution of the corresponding ligand, maintaining the molar ratio of  $\text{Co}:\text{L}(\text{L}=\text{phen} \text{ or } \text{bipy})$  at 1:2.

The compounds were found to be stable for a prolong period. They have been characterised from the results of elemental analyses, pyrolysis at  $120^\circ\text{C}$ , magnetic susceptibility measurements, i.r., laser Raman(LR), and electronic spectroscopic studies. The results suggest that each of the complexes described herein has a distorted octahedral structure. Whereas the binary fluoro-complexes of cobalt(II) have low magnetic moments, the mixed-fluoro complexes of the metal generally exhibit normal magnetic moments expected for high-spin  $d^7$  octahedral or distorted octahedral complexes of cobalt(II). This, therefore, demonstrates that a large antiferromagnetic interaction operative in the binary fluoro-complexes of cobalt(II) is controlled in the corresponding mixed-ligand fluoro-complexes of the metal.

While the interaction of  $[\text{CoF}_2(\text{N}_2\text{H}_4)_2] \cdot 2\text{H}_2\text{O}$  with acetylacetone afforded  $\text{Co}(\text{dmpz}')$  ( $\text{dmpz}' = \text{dmpz} - \text{H}$ ), the reaction of bis(acetylacetonato)cobalt(II) dihydrate,  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  with  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  and aqueous hydrofluoric acid produced  $[\text{Co}(\text{dmpz})\text{F}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ . These results suggest that the coligand  $\text{dmpz}$  can also be synthesised on a metal starting from the corresponding acetylacetonato compound besides providing an alternative route to the mixed-fluoro cobalt(II) species as obtained.

Chapter 4 of the thesis describes a new direct route to the synthesis of pure potassium trifluorocuprate(II),  $\text{KCuF}_3$ , as well as the synthesis and structural assessment of new mixed-ligand fluorocuprates(II),  $\text{A}[\text{CuF}(\text{SO}_4)] \cdot n\text{H}_2\text{O}$  ( $\text{A} = \text{Na}$ ,  $n=2$ ;  $\text{A} = \text{K}$  or  $\text{NH}_4$ ,  $n=3$ ).

White crystalline potassium trifluorocuprates(II),  $\text{KCuF}_3$ , has been synthesised directly from the reaction of  $\text{Cu}(\text{OH})_2$  with a small amount of 40% HF and potassium hydrogenfluoride,  $\text{KHF}_2$ , maintaining the molar ratio of  $\text{Cu}:\text{KHF}_2$  as 1:2 at  $\text{pH} < 4$ . Similar reactions at  $\text{pH} > 4$  resulted in contamination of the product suggesting thereby that high concentrations of both  $\text{H}^+$  and  $\text{F}^-$  are necessary to afford pure  $\text{KCuF}_3$ .

The synthesis of blue fluoro(sulphato)cuprates(II),  $\text{A}[\text{CuF}(\text{SO}_4)] \cdot n\text{H}_2\text{O}$  ( $\text{A} = \text{Na}$ ,  $n=2$ ;  $\text{A} = \text{K}$  or  $\text{NH}_4$ ,  $n=3$ ), has been accomplished by reacting  $\text{Cu}(\text{OH})_2$  with  $\text{AF}$  and  $\text{A}_2\text{SO}_4$  ( $\text{A} = \text{Na}$ ,  $\text{K}$  or  $\text{NH}_4$ ), in the molar ratio of  $\text{Cu}:\text{F}^-:\text{SO}_4^{2-}$  as 1:1:1, in the presence of a small amount of 40% HF at  $\text{pH} < 4$ . The reactions were

conducted at a steam-bath temperature. Attempted synthesis of the above complex species by alternative methods involving reactions among  $\text{Cu}(\text{OH})_2$ ,  $\text{F}^-$ , and  $\text{SCN}^-$  and  $\text{H}_2\text{O}_2$ , or  $\text{SO}_2(\text{g})$  and  $\text{H}_2\text{O}_2$ , gave mainly  $\text{CuSCN}$  and  $\text{Cu}(\text{II})[\text{Cu}(\text{I})\text{SO}_3]_2 \cdot 2\text{H}_2\text{O}$ , respectively, instead of the desired product. The compounds have been characterised on the basis of the results of chemical analyses, chemical determination of oxidation state of the metal, magnetic susceptibility and ESR measurements, i.r., laser Raman(LR) and electronic spectroscopic studies. The results of physical studies provide evidence for a distorted octahedral environment of  $\text{Cu}(\text{II})$  in the complex  $[\text{CuF}(\text{SO}_4)]^-$  species with a polymeric structure containing both  $\text{F}^-$  and  $\text{SO}_4^{2-}$  as bridging ligands. Further, strong antiferromagnetism operative in the binary fluorocuprate(II),  $\text{KCuF}_3$ , has been observed to be considerably controlled in the mixed-fluoro(sulphato)cuprates(II),  $\text{A}[\text{CuF}(\text{SO}_4)] \cdot n\text{H}_2\text{O}$ , as a result of partial replacement of two  $\text{F}^-$  ligands by one  $\text{SO}_4^{2-}$  in going from  $\text{CuF}_3^-$  to  $[\text{CuF}(\text{SO}_4)]^-$ .

Reported in Chapter 5 are a new general method of synthesis of bis(acetylacetonato)cobalt(II) dihydrate,  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , and bis(acetylacetonato)copper(II) dihydrate,  $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , and an interpretative account of the results of electron-ionisation mass spectrometric studies of the two compounds. Besides these, a comparative study of EI-induced mass spectra of acetylacetonates of first-row (3d) transition metals has been made.

The new general method for the synthesis of  $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$

and  $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  has shown that the compounds are capable of being synthesised in very high yields directly from the reaction of the corresponding metal hydroxide,  $\text{M}(\text{OH})_2$  ( $\text{M}=\text{Co}$  or  $\text{Cu}$ ), with acetylacetonone. The pH of the reaction solution was recorded, immediately after formation of the compounds to be **Ca.5**. The method does not require any buffer or alkali.

The electron-ionisation mass spectra of  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$  and  $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$  suggest that each of the two compounds exists as a monomer in the gaseous state and does not undergo any association. From the results of mass spectrometric investigations on  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$  and  $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$  and a comparison of the results with those of acetylacetonato compounds of manganese(II), iron(II), and nickel(II), it has been inferred that mass spectrometrically, bis(acetylacetonato)metal(II) compounds,  $\text{M}(\text{C}_5\text{H}_7\text{O}_2)_2$ , may be classified into two groups with  $\text{M}=\text{Mn}$ ,  $\text{Fe}$  or  $\text{Co}$  forming one, and  $\text{M}=\text{Ni}$  or  $\text{Cu}$  the other. Hydrogen atom migration from the ligand to the metal centre, as observed in the cases of  $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$  and  $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ , is significant. An alternative explanation for the hydrogen atom transfer has been provided.

Chapter 6, indeed the concluding Chapter of the thesis, presents the details of synthesis, characterisation, structural assessment, and some reactivity of peroxo-copper(II) complexes,  $[\text{Cu}_2(\text{OH})(\text{O}_2)(\text{H}_2\text{O})_2]\text{F}$  and  $[\text{Cu}_2(\text{OH})(\text{O}_2)(\text{H}_2\text{O})_2]_2\text{SO}_4$ . This chapter also gives an account of alternative routes to the synthesis of

Chevreur's salt,  $\text{Cu(II)[Cu(I)SO}_3\text{]}_2 \cdot 2\text{H}_2\text{O}$ , that were developed as a sequel to the study of reactivity of the peroxy-copper(II) complex cation  $[\text{Cu}_2(\text{OH})(\text{O}_2)(\text{H}_2\text{O})_2]^+$ .

Novel binuclear copper(II)-peroxy complexes,  $[\text{Cu}_2(\text{OH})(\text{O}_2)(\text{H}_2\text{O})_2]\text{F}$  and  $[\text{Cu}_2(\text{OH})(\text{O}_2)(\text{H}_2\text{O})_2]_2\text{SO}_4$ , have been synthesised from the reaction of  $\text{Cu(OH)}_2$  with minimum amounts of 40% HF and concentrated  $\text{H}_2\text{SO}_4$  respectively, and  $\text{H}_2\text{O}_2$  at pH 8-9 maintained by the addition of aqueous ammonia. These stoichiometric peroxy-compounds have been obtained for the first time in the solid state from the direct interaction of copper(II) with  $\text{H}_2\text{O}_2$ . The compounds have been characterised from the results of elemental analyses, red-ox titrations, magnetic susceptibility and ESR measurements, i.r. and laser Raman(LR) spectroscopy. The complex  $[\text{Cu}_2(\text{OH})(\text{O}_2)(\text{H}_2\text{O})_2]^+$  ion contains two Cu(II) atoms held together by a peroxide and a hydroxide groups, with the contiguous binuclear complex species being bonded to each other through bridging aqua groups, enabling each metal centre to be four coordinated, in the crystal lattice. The results of initial studies also show that the complex is a potential oxidant. The reaction of  $[\text{Cu}_2(\text{OH})(\text{O}_2)(\text{H}_2\text{O})_2]\text{F}$  in acetonitrile with  $\text{SO}_2(\text{g})$  affords an unusual red compound, in addition to hydrated copper(II)sulphate. The results of chemical and physico-chemical studies define the red compound to be  $\text{Cu(II)[Cu(I)SO}_3\text{]}_2 \cdot 2\text{H}_2\text{O}$ , the Chevreul's salt. As a sequel to this, two new straight forward methods for the synthesis of Chevreul's salt,  $\text{Cu(II)[Cu(I)SO}_3\text{]}_2 \cdot 2\text{H}_2\text{O}$ , have been developed. The chosen synthetic

strategies also enabled Etard's salt,  $\text{Cu}_2\text{SO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , to be obtained in a pure form as an intermediate product. Yellow Etard's salt,  $\text{Cu}_2\text{SO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , and red Chevreul's salt,  $\text{Cu(II)[Cu(I)SO}_3\text{]}_2 \cdot 2\text{H}_2\text{O}$ , have been obtained, at successive stages, from the reaction of cupric acetate or freshly prepared  $\text{Cu(OH)}_2$ , with  $\text{SO}_2(\text{g})$  in an aqueous medium. Characterisation of the compounds have been made from the results of chemical analyses, i.r. spectral and magnetic susceptibility measurements, and chemical reactions.

The work described in Chapter 4 and 5 and some parts of those incorporation in Chapters 3 and 6 have been published, while the rest is now under communication.

#### Chapter 3

J. Chem. Soc., Dalton Trans., 1987, 1055.

#### Chapter 4

Polyhedron, 1988, 7, 0000.

#### Chapter 5

Int. J. Mass Spectrom. Ion Processes, 1986, 71, 109.

#### Chapter 6

Ind. J. Chem., 1988, 27A, 0000.