CHAPTER-VI

COPPER(II), \( 3d^9 \)

1.1 INTRODUCTION,

1.2 EARLIER WORK,

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CHAPTER-IV

COPPER(II), 3d\(^9\)

1.1 INTRODUCTION:
Copper(II) is the third most abundant metallic element in the human body. Though trace amount of copper is essential for life and play an important role in the biochemistry of all living organism, it becomes toxic in large amount. Deficiency of copper in animals results in the inability to use iron stored in the liver. Thus animals become aneamic. It also occurs in all other forms of life and plays a role in the action of a multitude of enzymes\(^1\) that catalyze a great variety of reactions.
The accumulation of copper in the liver, kidneys and brain leads to Wilson's disease which is hereditary\(^2\). It can be treated by giving EDTA that formed complex with copper and are excreted in urine. In 2001 study of copper complexes has been driven by the hope of modeling\(^3\) biological molecules that contain copper.

Copper containing enzymes are studied in two ways:-

(1). According to the steric and spectroscopic characteristics of copper complexes at the active site.

(2). According to the function of the enzymes.

Haemocyanin is the copper containing respiratory enzymes, which is used as an oxygen carrier in some invertebrates (snails, crabs, lobsters, octopuses and scorpions). These are protein of high molecular weight but it consists of subunits\(^6\). Each subunit has one pair of copper atom and can bind with one oxygen molecule.
Oxygenated haemocyanins are blue in colour. There are several blue proteins which contain copper i.e. plastocyanin and azurin. Plastocyanin occurs in chloroplast of green plants which contains one copper atom, used in photosynthesis as an electron\textsuperscript{7,8} carrier. Azurin is found in bacteria.

Copper(II) is also used in the electrical industry because of its high conductivity. It is also used for water pipes because of its inertness. Copper compounds are also used in agriculture like Bordea mixture. This is an important spray for preventing fungus attack on the leaves of potato. Copper(II) is also used as an insecticide. The bleomycin is a group of glycopeptides isolated from Streptomyces Verticillus as copper complexes. They have much attention because in addition to having to antimicrobial and antiviral\textsuperscript{9,10} properties, it is also used in the treatment of a number of tumours, including Hodgkin’s disease.

Copper(II) affects enzymes activity both as a co-factor and as an allosteric component of cuperoenzymes including cytochrome-c-oxidase, super oxidase dismutase, dopamine-β-hydroxylase, lysyl oxidase, tyrosinase and cerulopalsmin\textsuperscript{11}. Copper(II) is essential for cellular respiration, neurotransmitter function, connective tissue biosynthesis, pigmentation and cellular iron metabolism. Excess amount of copper(II) is toxic in all the species. Copper(II) toxicity results from inherited abnormalities and leads to hepatic cirrhosis, hemolytic anemia and degeneration\textsuperscript{12,13,14} of basal ganglia. Wilson disease and Indian childhood cirrhosis (ICC) are the most common disorders of copper metabolism. Prasad et.al\textsuperscript{15} have suggested that the nucleus is the principal site of copper cytotoxicity.
1.2 EARLIER WORK ON COPPER(II) COMPLEXES:

Cu(II) and Ni(II) complexes of benzyl methyl and methyl-n- hexyl ketones thiosemicarbazones were synthesized by Chandra et.al\textsuperscript{16}. These complexes were found to have ML\textsubscript{2} composition. All the complexes have been characterized by magnetic moment measurement, IR, electronic and ESR spectral studies. All the complexes were found to have four coordinated square planar geometry. Cu(II) complexes of 2-hydroxyacetophenone and 2-hydroxynaphthaldehyde semicarbazones have been synthesized by Chandra et.al\textsuperscript{17}. The complexes were found to have [Cu(L)X] composition, where X = Cl, Br, NO\textsubscript{3}, ClO\textsubscript{4}, CH\textsubscript{3}COO. Both the ligands behave as tridentate. All the complexes were found the have square planar geometry.

Sharma et.al\textsuperscript{18} synthesized Cu(II) complexes with isobutyl methyl ketone semicarbazone. The complexes have the general compositions[Cu(L\textsubscript{2}X\textsubscript{2})] and [Cu (L\textsubscript{2}X\textsubscript{2})].2H\textsubscript{2}O compositions. The complexes were characterized by magnetic moments, IR electronic and ESR studies. The electronic and ESR spectral data suggest a five coordinated trigonal bipyramidal geometry for the [Cu(L\textsubscript{2}X\textsubscript{2})] complex and six coordinated octahedral geometry for [Cu(L\textsubscript{2}X\textsubscript{2})].2H\textsubscript{2}O.

Cu(II) and Pd(II) complexes of propiophenone and butyrophenone thiosemicarbazones have been synthesized by Chandra et.al\textsuperscript{19}. These complexes were characterized by magnetic moments, IR electronic and ESR spectral studies. The complexes were found paramagnetic and have square planar geometry.
Cu(II) complexes of 1-(2-naphthylacetyl)-4-phenyl-3-thiosemicarbazone have been prepared by Bekheit et al.\textsuperscript{20}. The complexes were characterized by magnetic moments, IR electronic and ESR spectral studies. Square planar geometry was proposed for all the complexes. Two Cu(II) complexes i.e. chlorobis (triphenylphosphine) and chlorobis (methylpyruvate) thiosemicarbazones have been prepared by Balicchif et al.\textsuperscript{21}. These complexes were characterized by spectroscopic studies and single X-ray diffraction method.

Cu(II) complexes of 3,4-dimethoxybenzaldehyde thiosemicarbazone have been prepared by Balakrishnan et al.\textsuperscript{22}. The complexes were found to have Cu(LH)\textsubscript{n}X\textsubscript{2}, CuL\textsubscript{2} and CuLHCl compositions, where X = Cl\textsuperscript{-}, Br\textsuperscript{-}, I\textsuperscript{-} and n = 1, 2. These were characterized by elemental analysis, molar conductance, magnetic moments and electronic, IR and NMR spectral studies. Cu(II) complexes of o-hydroxy acetophenone semicarbazone have been synthesized by Soliman et al.\textsuperscript{23}. These were characterized by elemental analysis, molar conductance, magnetic moment, electronic, IR and NMR spectral studies.

Scovill et al.\textsuperscript{24} prepared Cu(II) complexes of 3-acetylisoquinoline thiosemicarbazone. These were characterized by elemental analysis, physical and spectral (Mass, IR, Electronic, ESR) studies. The complexes possess antifungal activities. Cu(II) complexes of 2-formylimidazole \textsuperscript{4}N-methyl, \textsuperscript{4}N-dimethyl, \textsuperscript{4}N-ethyl and 3-hexamethyleneiminyl thiosemicarbazones have been synthesized by West et al.\textsuperscript{25}. Electronic, IR, NMR, ESR spectral data have been used to characterized all the complexes. All the complexes possess growth inhibitory activity against Aspergillus niger and Paecilomyces Varioti.
Cu(II) complexes show either modest or no growth inhibitory activity against *Paecilomyces variotii*. Cu(II) complexes of semicarbazones derived from isoatin, benzoin and 2-hydroxynapthaldehyde were also synthesized by West et al.\textsuperscript{26}. These were characterized by IR, electronic, ESR, \textsuperscript{1}H and \textsuperscript{13}C NMR spectral studies.

Cu(II) complexes of 6-methyl-2-formyl-pyridine thiosemicarbazone and its \textsuperscript{4}N-methyl, \textsuperscript{4}N-ethyl, \textsuperscript{4}N-phenyl, \textsuperscript{4}N-dimethyl, \textsuperscript{4}N-diethyl, \textsuperscript{4}N-dipropyl, 3-pyrrolidinyl, 3-piperidinyl and 3-hexamethylene isothiosemicarbazone derivatives and 2-formyl pyridine, 3-piperidinyl-3-hexamethylenemimyl and 3-azabicyclo [3.2.2] nonyl thiosemicarbazones were also prepared by West et al.\textsuperscript{27-28}. These were characterized by electronic, ESR and \textsuperscript{1}H,\textsuperscript{13}C NMR spectral studies. New Cu(II) complexes with pyridoxyl N-(4)-methylthiosemicarbazone, N-(4)-ethyl thiosemicarbazone, N-(4)-phenyl thiosemicarbazone have been prepared by Mohan et al.\textsuperscript{29}. All the complexes were characterized by elemental analysis, IR and ESR spectral studies.

Grafine et al.\textsuperscript{30} have synthesized three types [Cu (apmt)Cl\textsubscript{2}], [Cu (apmt) Cl] Cl and [Cu\textsubscript{2}(pgmt)Cl\textsubscript{2}]Cl\textsubscript{2} complexes with 2-acetylpyridine-2-methyl-3-thiosemicarbazone and di-2-pyridylglyoxal-bis-2-methyl-3-thiosemicarbazone. The tentative structures of the complexes were determined by using various spectral studies. The complexes were characterized by IR, \textsuperscript{1}H NMR, and electronic, molar conductance and magnetic moment measurements.

Cu(II) complexes of 6-methyl-2-acetylpyridine thiosemicarbazone have been prepared by West et al.\textsuperscript{31}. These complexes were characterized by IR, electronic,
EPR, $^1$H and $^{13}$C NMR spectral studies. Cu(II) complexes of 1-salicyl-4-phenyl thiosemicarbazone have been synthesized by Narayan et al. These complexes were characterized by elemental analysis, magnetic moment and ESR spectral studies. Cu(II) complexes of 5-bromosalicylaldehyde-2-methylthiosemicarbazone have been prepared by Valeds et al. These complexes were characterized by X-ray diffraction method. Cu(II) complexes of 4-formylantipyrine N-(4)-thiosemicarbazone have been synthesized by West et al. These complexes were characterized by IR, electronic, $^1$H and $^{13}$C NMR spectral studies.

A series of N-(4) substituted thiosemicarbazones of isatin and their Cu(II) complexes were synthesized by Bain et al. These complexes were characterized by elemental analysis, magnetic moment, and IR spectral studies. Cu(II) complexes of 2-formyl, 2-acetyl and 2-benzoylpyridine N-(4)-o-, N-(4)-m-, N-(4)-p-chlorophenyl thiosemicarbazones and formyl and acetylpyrazine N-(4)-2-methylpyridinyl N-4-2(ethylpyridinyl) and N-4-methyl-2-ethylpyridinyl thiosemicarbazones were also synthesized by West et al. These complexes were characterized by IR, electronic, ESR, $^1$H and $^{13}$C NMR spectral studies. Cu(II) complexes of the types [CuLX] and [Cu(NO$_3$)](HL)$_2$H$_2$O] synthesized with pyridine-2-carbaldehyde thiosemicarbazone by Gracia et al. The complexes were characterized by electronic, magnetic moments and X-ray diffraction methods.

Cu(II) complexes of 4-acetamidobenzaldehyde N-(4)-thiosemicarbazone have been synthesized by West et al. These complexes were characterized by
physical and spectral techniques. Cu(II) complexes of furan-2-carboxyaldehyde and methyl-2-thienyl ketone semicarbazones and thiosemicarbazones have been synthesized by Reddy et al. All the complexes were characterized by IR, ESR and electronic spectral studies. Mamashvili et al. prepared Cu(II) complexes of methyl-glyoxal thiosemicarbazone. The reduction of Cu(II) to Cu(I) was confirmed by ESR. Theses complexes were characterized by UV, IR and NMR spectral studies.

Cu(II) complexes of 4-[N-2-hydroxy-1-naphthalidine]-amino] antipyrine thiosemicarbazone have been synthesized by Chopra et al. These complexes were characterized by elemental analysis, magnetic moment, molecular weight, IR and electronic spectral studies. Cu(II) complexes with furan semicarbazone in ethanolic solution have been synthesized by Ibrahim et al. These complexes were investigated for their cytotoxic activities. Cu(II), Zn(II) and Cd(II) complexes of salicylaldehyde -4-, 4- dimethyl -3-thiosemicarbazone have been synthesized by Choudhary et al. They have the general composition [M (saldmstsc) n. H2O]. Where n = 0 or 1. Cu(II) complexes of 2-pyridineformamide N-(4)-methyl thiosemicarbazone have been synthesized by West et al. Cu(II) complexes have been characterized by molar conductivity, magnetic susceptibility and spectroscopic techniques.

1-isonicotinoyl-4-benzoyl-3-thiosemicarbazone (IBtsc) and its Fe(II), Cu(II) and Zn(II) complexes have been prepared by Singh et al. These complexes were characterized by elemental analysis, magnetic susceptibility measurements U.V,
I.R, N.M.R and F.A.B mass spectral data. The c.s.r spectra of the Fe(II) and Cu(II) complexes show tetrahedral and square pyramidal geometry respectively. Ibts and its soluble complexes have been screened against several bacteria, fungi and tumour cell lines. Ni(II) and Cu(II) complexes of di-2-pyridyl ketone N-(4)-methyl- and N-(4)-dimethyl-thiosemicarbazones have been synthesized by West et al. These complexes were characterized by physical and spectral methods.

Cu(II), Ni(II) and Zn(II) complexes of 3-acetylbemelliferon thiosemicarbazones (HL) were synthesized by Wang et al. The complexes have the general composition [ML₂]n H₂O, where n=0, 2. The ligand and its complexes have been screened for their possible antitumor activity against HL-60 human leukemia in vitro. Cu(II) complexes of the types [Cu(NNS) NO₃] H₂O and [Cu(NNS)₂] with 6-methyl-2-formylpyridine N-4-dimethyl thiosemicarbazone have been synthesized by Ali et al. All the complexes were characterized by physico-chemical techniques, such as magnetic moment and spectroscopic spectral studies. On the basis of above spectral data five coordinated structure may be suggested for [Cu(NNS)NO₃]H₂O]H₂O. Cobalt (II) and copper (II) complexes of di-2-pyridyl ketone 3-piperidyl and 3-hexamethyllenciminyl thiosemicarbazone have been prepared by West et al.

Copper(II) complexes of 2-benzoyl pyridine N-(4), N-(4)-(butane-1,4-dyl) thiosemicarbazone have been synthesized by Kurup et al. The complexes were characterized by IR and UV. The general composition [CuBpypTscX], where X=Cl, NO₃, NCS, ClO₄, Br and CN. Cu(II) complexes of 1-phenyl-1, 2-
propanedione-2-oxime thiosemicarbazone have been synthesized by Reddy et al. The reaction products so obtained are coloured. These coloured reaction products have been advantageously used for the simultaneous spectrophotometric determination and also used in edibles oils and seeds.

Cu(II) and Zn(II) complexes of vitamin K₃ thiosemicarbazone have been synthesized by Tang et al. These were characterized by elemental analysis, IR, molar conductance and thermal analysis. All the complexes possess strong inhibitory action against G (+) staphylococcus aureus, G (-) Hay basicillus, and G (-) Escherichia coli. The antibacterial activities of the complexes were stronger than those of the thiosemicarbazone itself.

Co(II) and Cu(II) complexes of 2-pyridineformamide-N-(4)-dimethyl thiosemicarbazone have been synthesized by Castineiras et al. They have the general compositions [M(Am4DM)OAc] and [M(Am4DM)OAc]), (where M=Co and Cu). These were characterized by spectroscopic techniques. Ansari et al. reported Cu(II) complexes of 2-amino-4-benzamido thiosemicarbazone. All the complexes were found paramagnetic with an octahedral geometry.

Complexes of Copper(II) were synthesized with salicylaldehyde semicarbazone by Yang et al. These were characterized by range of physicochemical techniques. 2, 6- diacetyl and 2, 6- diformylpyridine bis (N-4- substituted thiosemicarbazones) and their copper(II) complexes have been synthesized by West et. al. Cu(II) complexes of N-N’-bis (salicylidene) thiosemicarbazone were synthesized by Yildiz et al. These complexes were characterized by the
elemental analysis, magnetic susceptibility measurements, $^1$H NMR, IR, and UV-visible spectral data which suggest an octahedral geometry for Cu(II) complexes.

The antibacterial activity of the ligand and the metals complexes was screened in the vitro against the organism Escherichia coli, Staphylococcus aureus, Bacillus cereus, and Prteus vulgaris. It had been observed that the coordination of the metal ions has pronounced effects on the microbial activities of the ligands.

Cu(II) complexes of 4-hydroxy -1- phenyl quinolin 2(1H) one-semicarbazone (HPQS=HL$_1$) and 4-hydroxy 1- phenyl quinolin -2(1H) one thiosemicarbazone (HPQTS=HL$_2$) have been prepared by Rai et.al$^{59}$. These complexes were found to have the general composition [M(HPQS)$_2$] and [M(HPQTS)$_2$], where M = Cu(II). These were characterized by elemental analyses, magnetic susceptibility, molar conductance, infrared spectra and electronic spectra. Cu(II) react with Schiff bases viz. bis-(cinnamaldehyde)semicarbazone (CSCZ), bis-(4-hlorobenzaldehyde) semicarbazone (CBSCZ), bis-(3,4,5-trimethoxybezaldehyde semicarbazone (TMBSCZ), bis-(pyridine-2-aldehyde) semicaebazone (PASCZ), and bis-(thiophene-2-aldehyde)semicarbazone) (TASCZ). These complexes were synthesized by Ahmad et.al$^{60}$. All the complexes were screened for their antimicrobial activity by agar disc diffusion method against the bacteria X. citri and the fungi A. soleni. All the complexes exhibit an octahedral geometry.

Giles et.al$^{61}$ prepared Cu(II) and Ni(II) complexes with 2-acetyl-2-thiazoline semicarbazone (ATSC). The metal complexes have the general compositions [CuCl$_2$(ATSc)] and (Ni(ATSc)$_2$)(NO$_3$)$_2$.2H$_2$O. These were characterized by
 elemental analysis, IR, UV and magnetic susceptibility. Electrochemical behavior of some Cu(II) thiosemicarbazone complexes have been investigated by El-Shahawi et al.\textsuperscript{62}

The synthesis of Ni(II), Cu(II) and Cd(II) complexes of 3-furaldehyde thiosemicarbazone (3FTSc) were reported by Bouet et al.\textsuperscript{63} Elemental analysis, molar conductance and spectral (IR, UV and \textsuperscript{1}H NMR) measurements have been used to characterize the complexes. In Cu(II) and Ni(II) complexes, the metal ion is coordinated through the sulphur atom and the azomethine nitrogen atom. Cu(II) complexes of naphthoquinone thiosemicarbazone have been synthesized by West et al.\textsuperscript{64} These complexes were characterized by elemental analysis, EPR and molar conductance etc.

Cu(II) complexes of imidazole-2-carbaldehyde, pyrrole-2-carbaldehyde and indole-3-carbaldehyde thiosemicarbazones were synthesized by Arguelles et al.\textsuperscript{65} The antimicrobial properties of the free ligands and their complexes were evaluated against yeast, mould and bacteria G(+) and G(-). Some copper chelates exhibited a moderate inhibitory activity than that of the corresponding free ligands. The pyrrole derivative [Cu(HL\textsubscript{2})\textsubscript{2}], show an interesting inhibition of the growth of all G(+) bacteria and fungi. Cu(II) complexes of di-2-pyridyl ketone N-(4)-methyl, N-(4)-phenyl thiosemicarbazone have been synthesized by Kurup et al.\textsuperscript{66} These complexes were found [Cu(dptsc)Cl\textsubscript{2}]\textsubscript{2}3H\textsubscript{2}O (i)[Cu(dptsc)Br\textsubscript{2} (2).[Cu(dptsc)(\textmu-N\textsubscript{3})] (3).[Cu( dptsc)NO\textsubscript{3}]\textsubscript{2}2H\textsubscript{2}O, where (dptsc=di-2-pyridyl ketone N-(4)-methyl, N-(4)-phenyl thiosemicarbazone) compositions. Cu(II)
complexes of 2-acetylpyrrole thiosemicarbazone (H$_2$L$_1$) and 2-acetylfuran thiosemicarbazone (HL$_2$) have been synthesized by Youssef et al.$^{67}$ These complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility and IR spectral studies. Cu(II) complexes of 2-[E-(5-phenyl-6H-1,3,4-thiadiazin-2yl)imino]methyne)-1-naphthol(L$_1$H) and 5-nitro-2-[5-phenyl-6H-1,3,4-thiadiazin-2-yl)imino] methyne) phenol(L$_2$H) have been synthesized by Aysegul et al.$^{68}$ The structure of the ligands and their complexes were identified by using elemental analysis, IR, NMR, electronic, magnetic susceptibility measurements and by the help of thermo-gravimetric analysis. Cu(II) complexes of [2-hydroxy-1-naphthalddehyde]-3-isatin] bishydrazone have been synthesized by Mohanan et al.$^{69}$ These complexes were characterized by elemental analysis, molar conductance, and magnetic susceptibility IR, ESR and NMR spectral studies. Antibacterial tests of the ligand and the metal complexes showed that the complexes were more potent bactericides than the ligand. Cu(II) complexes of embelinesemicarbazone were synthesized by Alaudeen et al.$^{70}$ These were characterized by UV, IR and $^1$HNMR spectral studies. Copper(II) complexes of salicylaldehyde semicarbazone has been synthesized by Yang et al.$^{71}$ These complexes were characterized by physico-chemical techniques. Ni(II), Zn(II), Cu(II) and Hg(II) complexes of cis-3, 7- dimethyl-2, 6-octadien semicarbazone have been synthesized by Nagar et al.$^{72}$ The complexes were found to have the general compositions [ML$_2$Cl$_2$] and [ML$_2$]Cl$_2$. The
possible geometry may be assigned on the basis of elemental analysis, molar conductance, magnetic measurements, IR and electronic as well as N.M.R spectral data. All the complexes as well as ligand were screened for their antibacterial activity. All the complexes exhibit strong inhibitory action against Gram (+) bacteria Staphylococcus aureus, and G (-) bacteria Escheriachia Coli. The antibacterial activities of the complexes are stronger than those of the ligand itself. Cu(II) complexes of 3-hydroxybenzaldehyde thiosemicarbazone have synthesized by Reddy et.al\textsuperscript{73}. The reagent gave yellow coloured complexes with copper (II). These coloured reactions were used in the spectrophotometric determination of copper (II) in aqueous medium.

Copper(II) complexes of 2-benzoyl pyridine N-(4)-phenyl thiosemicarbazone have been synthesized by Kurup et.al\textsuperscript{74}. These complexes were characterized by molar conductivity, measurements, magnetic studies, electronic, infrared and EPR spectral studies. Cu(II) complexes of 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone (ppdot) have been prepared by Reddy et.al\textsuperscript{75}. These complexes were characterized by spectrophotometric method. Cu(II) complexes of malonyl bis-(thiosemicarbazone) were synthesized by El-Asmy et.al\textsuperscript{76}. These complexes were characterized by elemental analysis, magnetic moments, UV.IR, ESR spectral studies. Cu(II) complexes of di-2-pyridyl ketone N-(4), N-(4)-(butane-1, 4-diyl) thiosemicarbazone have been synthesized by Kurup et.al\textsuperscript{77}. These complexes were characterized by elemental analysis, magnetic moments, UV.IR, ESR.spectral studies
1.3 PRESENT WORK:
The present work is related to the synthesis and characterization of copper(II) complexes with four ligands [pvsc (L\textsuperscript{1}), pvts (L\textsuperscript{2}), ptasc (L\textsuperscript{3}) and ptatsc (L\textsuperscript{4})]. These complexes were characterized by the elemental analysis, molar conductance, magnetic moment, I.R and electronic spectral studies.

![Structure of ligands](image)

On the basis of elemental analysis the complexes were found to have general composition Cu\textsubscript{2}L\textsubscript{x}X\textsubscript{y} (where L\textsuperscript{x} = (L\textsuperscript{1}), pvts (L\textsuperscript{2}), ptasc (L\textsuperscript{3}) and ptatsc (L\textsuperscript{4}); X\textsuperscript{y} = Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and CH\textsubscript{3}COO\textsuperscript{-}). The molar conductance of these complexes has been determined in DMSO solution. Molar conductance indicates that the bromo and sulphato complexes with pvsc, pvts, ptasc and ptatsc and nitro complexes are non-electrolyte in nature whereas nitro and acetate complexes with pvsc, pvts, ptasc are 1:2 electrolyte in nature. So the formular of complexes may be [Cu(L\textsubscript{x})X\textsubscript{y}] \textsuperscript{2+}, [Cu(L\textsubscript{x})] X\textsubscript{y} and [Cu(L\textsubscript{x})] X\textsubscript{y} respectively (Table 1).
PREPARATION OF THE COMPLEXES:
A hot ethanolic solution (20mL) of the corresponding copper salt (.05 mole) was mixed to a hot ethanolic solution of the ligand (.01 mole). The mixture was refluxed on a water bath for about 6-8 hrs at 70-80°C. After refluxing the mixture, it was concentrated to half of its volume. On cooling in a refrigerator the coloured crystals of the complexes precipitated out. It was filtered, washed with 50% ethanol and dried in an electric oven at 70°C. (Yield 65-80%).

1.4 RESULT AND DISCUSSION:
On the basis of elemental analysis the complexes were found to have general composition Cu(L)_2X_2 (where L = (L^1), pvtsc (L^2), ptasc (L^3) and ptasc (L^4), X = Cl, -NO_3, 1/2SO_4^2- and CH_3COO^-). The molar conductance of these complexes has been determined in DMSO solution. Molar conductance indicates that the chloro and sulphato complexes with pvsc, pvtsc, ptasc and ptatsc and nitrato complex with ptatsc are non-electrolyte in nature. Whereas nitrato and acetato complexes with pvsc, pvtsc, ptasc are 1:2 and 1:1 electrolyte in nature respectively. So the formulae of complexes may be [Cu(L)_2X_2], [Cu(L)_2] X_2 and [Cu(L)_2 X]X respectively. Table-1.

IR SPECTRA
The IR spectra of all the ligands and their metal complexes have already been discussed in the previous chapter II.
BANDS DUE TO ANIONS:

IR SPECTRA OF THE NITRATO COMPLEXES

The spectra of nitrato complexes of Cu(II) with pvstc, ptstc and ptasc indicate that the nitrato group is uncoordinated as the band of free nitrate is present in the region of 1380-1385 cm\(^{-1}\) [Figs-5.1, 5.2, 5.3].

The IR spectrum of the nitrate complex of ptatstc shows absorption bands in the region of 1448 cm\(^{-1}\) (\(v_3\)) \(v_s(\text{NO}_2)\), 1305 (\(v_1\)) \(v_s(\text{NO}_2)\) and 854 cm\(^{-1}\) (\(v_2\)) \(v(\text{NO})\).

This indicates the unidentate coordination of nitrato group\(^{78}\).

IR SPECTRA OF SULPHATO COMPLEXES:

The IR spectra of the sulphato complexes of pvstc, ptstc, ptasc and ptatstc show absorption bands in the region of 1113-1104 cm\(^{-1}\) (\(v_3\)), 1076-1039 cm\(^{-1}\) (\(v_3\)), and 735-652 cm\(^{-1}\) (\(v_4\)) corresponding to unidentate sulphate [Fig-5.4] group.

IR SPECTRA OF ACETATOTO COMPLEXES:

According to Nakamato\(^{78}\) the free acetate ion of \(v_s(\text{COO}^-)\) and \(v_a(\text{COO}^-)\) are present at 1560 and 1416 cm\(^{-1}\). The separation between \(v_a\) and \(v_{as}\) was observed around 150 cm\(^{-1}\). However, if the acetate acts as unidentate ligand then \(v(C=O)\) is present at higher position than \(v_s(\text{COO}^-)\) and \(v(C-O)\) in lower position than \(v_s(\text{COO}^-)\). Therefore separation between \(v_a\) and \(v_{as}\) is much larger in unidentate complexes than in the free ion.

But in bidentate complexes the separation between the two \(v(C-O)\) is smaller than
Figure 5.2 IR Spectrum of [Cu (pvtsc)$_2$] (NO$_3$)$_2$
**Figure 5.3 IR Spectrum of [Cu (ptasc)$_2$] (NO$_3$)$_2$**

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<th>Wavenumber (cm$^{-1}$)</th>
<th>Peak Height (arb. units)</th>
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Figure 5.5 IR Spectrum of [Cu (pivsc)$_2$(SO$_4$)$_2$]
that of the free ion.

The IR spectra of acetato complexes under study of pvsc, pvts, ptase and ptatse show bands near 1539 and 1448 cm\(^{-1}\). These bands may be assigned to \(\nu(C=O)\) and \(\nu(C-O)\). The difference of above two bands is 39-50 cm\(^{-1}\). It indicates that in the present study acetate group acts as bidentate ligand.

**MAGNETIC MOMENT**

Magnetic moments of all the complexes at room temperature lie in the range 1.82 - 2.00 B.M., corresponding to one unpaired electron. Although the theory suggests that there should be some co-relation between the magnitude of orbital contribution and the coordination geometry. In practice it is not observed, presumably because of distortion and other variables like covalence. Only if there is antiferromagnetic interaction between copper pairs, in which case lower magnetic moments or even diamagnetic results. The data in the present complexes shows absence of such interactions.

**ELECTRONIC SPECTRA**

The electronic spectra of six-coordinate Cu(II) complexes have either D\(_{4h}\) or C\(_{4v}\) symmetry. The ground state in an octahedral field is the \(^2E_g\).

According Hathaway very few regular octahedral Cu(II) complexes were known\(^{79}\). In an octahedral field if the \(E_g\) and \(T_{2g}\) separation varies from 13000-18000 cm\(^{-1}\) results distortions.
Because of Jahn-Teller effect operating on the $^2E_g$ ground term of an octahedron, distortions will occur. It is useful to define a tetragonality factor $T$ (where $T =$ in plane Cu-L distance/ mean out of plane Cu-L distance). In general $T$ may be less than one or greater than one. Thus due to distortions a several absorption bands may be expected in these regions.

The $E_g$ and $T_{2g}$ levels of the $^2D$ free ion term will split into $B_{1g}, A_{1g}, B_{2g}$ and $E_g$ levels respectively. Thus three spin-allowed transitions are expected in the visible and near IR region though they may not always be resolved. But only a few complexes are known in which such bands are resolved either by “Gaussian Analysis” or by “Single crystal polarization” studies.

These bands have been assigned to the following transition in order of increasing energy:

$$^2A_{1g} \leftarrow ^2B_{1g} (a_{1g}^2 . b_{1g}^1 . \rightarrow a_{1g}^1 . b_{1g}^2)$$

$$^2E_g \leftarrow ^2B_{1g} (e_g^4 . a_{1g}^2 . b_{1g}^1 . \rightarrow e_g^3 . a_{1g}^2 . b_{1g}^2)$$

**Electronic Spectra Of Cu(II) Complexes of pvse, pvtse and ptasc:**

The electronic spectra of the complexes having molecular formula Cu(L)$_2$X$_2$ (where $X =$ Cl$^-$) show two bands in the range of 15105-15432 and 16067-16341 cm$^{-1}$. The position of these bands suggests that these complexes have tetragonal geometry.
Electronic Spectra Of Cu(II) Complexes of pvsc, pvts, ptsc and ptats:
The electronic spectra of acetato complexes with all the ligands show two absorption bands in the range of 13700-14000 and 16220-16600 cm\(^{-1}\). These bands suggest six co-ordinated geometry.

Electronic Spectra of Cu(II) Complexes of pvsc, pvts and ptsc:
Since the nitrate group is unco-ordinated therefore four co-ordinated geometry may be assigned to these complexes. The electronic spectra of nitrate complexes with pvsc, pvts and ptsc ligands show two bands in the range of 14004-14500 and 16168-16500 cm\(^{-1}\), corresponds to square planar geometry\(^{79, 80}\).

Electronic Spectra Of Cu (II) complex of ptats:
The electronic spectrum of nitrate complex with ptats ligand shows two bands in the range of 10256, 13200 cm\(^{-1}\), which is corresponding to tetragonal geometry\(^{79}\).

Electronic Spectra of Sulphato Complexes with pvsc, pvts, ptsc and ptats:
Since the sulphato group is unidentate therefore five co-ordinated square pyramidal or trigonal bipyramidal geometry may be assigned to these complexes. Two bands in the range 13602-14778 and 16021-16471 cm\(^{-1}\) were observed in the electronic spectra of sulphato complexes with all the ligands. The position of these bands suggests square pyramidal geometry.
Figure 5.7 Electronic Spectrum of [Cu (pvsc)$_2$Cl$_2$]
Figure 5.9 Electronic Spectrum of [Cu (pvtsc)$_2$Cl$_2$]
Figure 5.8 Electronic Spectrum of [Cu (pvsc)$_2$(SO$_4$)]
Figure 5.10 Electronic Spectrum of [Cu (ptatse)$_2$(NO$_3$)$_2$]
EPR SPECTRA OF CHLORO, NITRATO AND ACETATO COMPLEXES:

Generally tetragonal Cu(II) complexes give anisotropic EPR spectra. The anisotropic g-values have been calculated by using the following expressions:

\[ g_\parallel = 2(1 - 4\lambda / \Delta E_2) \]

and \[ g_\perp = 2(1 - \lambda / \Delta E_3) \]

Where \( \lambda = 823 \text{ cm}^{-1} \) and \( \Delta E_2 = ^2B_{1g} \rightarrow ^2B_{2g}, \Delta E_3 = ^2B_{1g} \rightarrow ^2E_g \)

The stronger interaction along the ‘Z’ axis is to be accompanied by an increase in the value of \( g_\parallel \). The stronger axial bonding leads to an increase in the length of the bond in the XY plane, which results in a decrease of both in-plane covalency and energy of the \( d^2_{x^2-y^2} \rightarrow d_{xy} \) transition\(^{82,83}\). Both these factors tend to increase the value of \( g_\parallel \).

For the tetragonally elongated octahedral Cu(II) complexes, the g and A tensors are given by the usual axially symmetric spin Hamiltonian\(^{84}\).

\[
-H = \beta \left[ g_\parallel (B_x S_x) + g_\perp (B_x S_x + B_y S_y) + A_\parallel (S_z I_z) + A_\perp (S_x I_x + S_y I_y) \right]
\]

\[ g_\parallel = 0.0023 - 8\lambda (\alpha^2 \beta^2) / \Delta E \]

\[ g_\perp = 2.0023 - 2\lambda (\sigma^2 \gamma^2) / \Delta E \]

\[ A_\parallel = P \{-[\alpha^2 (4/7 + K)] - 2\lambda \alpha^2 [4\beta^2 / \Delta E + 3\gamma^2 / 14\Delta E \alpha^2]\} \]

Here \( \lambda \) is the spin orbit coupling constant which is -823 cm\(^{-1}\) for free Cu(II) ion and \( \Delta E \) is the energy difference between electronic energy states.
EPR SPECTRA OF SULPHATO COMPLEXES:

The two structures can be adopted i.e. trigonal bipyramidal and square pyramidal for sulphato complexes having coordination number five.

The square pyramidal and trigonal bipyramidal structures have ground state configuration $^2\!B_1$ (unpaired electron being in $d_{x^2-y^2}$ orbital) and $^2\!A_1$ (unpaired electron in $d_z^2$ orbital), respectively. The EPR prove to be good to distinguish between these two ground state terms. EPR spectra of sulphato complexes show $g_3 > g_2 > g_1$.

The ratio of $(g_2-g_1)/(g_3-g_2)$ called the parameter $R$, which is very useful to distinguish between square pyramidal and trigonal bipyramidal geometry.

If the ground state is $^2\!A_1$ the value of $R$ reported to be greater than one. If the value of $R$ is less than one, indicating $^2\!B_1$, as the ground state.

The value of $R$ for the complexes under study is found less than one and therefore the complexes may may have five coordinate square pyramidal geometry.

On the basis of aforesaid study such as elemental analysis, molar conductance measurements, magnetic susceptibility, IR, electronic and EPR spectral data, the following structures may be purposed for all the complexes.
Figure 5.12 EPR Spectrum of \([Cu\text{pris}e_2\text{Cl}]\)
\[ \text{[Cu(pvsc)$_2$Cl$_2$]} \]

\[ \text{[Cu(pvtsc)$_2$Cl$_2$]} \]

\[ \text{[L = ptasc and X = Cl]} \]
[L=pvsc, pvtscc and ptasc]

[(NO_3)_2]

[L= ptatsc, X= (NO_3)_2]
\[ L = \text{pvsc, pvtsc, ptasc and ptatsc,} \]
\[ X = \text{SO}_4 \]
[L = pvsc, pvtsc, ptasc and ptatsc,  
X = CH$_3$COO]
<table>
<thead>
<tr>
<th>Complexes</th>
<th>Colour</th>
<th>Yield %</th>
<th>Molar Conductance Ω Mole^2 cm^-1</th>
<th>Elemental analyses found and (calculated) %</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>[Cu(pvsc)_2 Cl_2]</td>
<td>Green</td>
<td>85</td>
<td>19</td>
<td>11.55 (11.49)</td>
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<tr>
<td>[Cu (pvsc)_2 Cl_2]</td>
<td>Dark Green</td>
<td>66</td>
<td>18</td>
<td>10.75 (10.86)</td>
</tr>
<tr>
<td>[Cu (ptasc)_2 Cl_2]</td>
<td>Shiny Green</td>
<td>70</td>
<td>17</td>
<td>12.79 (12.89)</td>
</tr>
<tr>
<td>[Cu (ptatsc)_2 Cl_2]</td>
<td>Heena Green</td>
<td>77</td>
<td>16</td>
<td>12.06 (12.10)</td>
</tr>
<tr>
<td>[Cu pvsc]_2)(NO_3)_2</td>
<td>Brown</td>
<td>80</td>
<td>170</td>
<td>10.39 (10.48)</td>
</tr>
<tr>
<td>[Cu pvsc]_2)(NO_3)_2</td>
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<td>89</td>
<td>168</td>
<td>9.17 (9.00)</td>
</tr>
<tr>
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<td>85</td>
<td>160</td>
<td>11.56 (11.64)</td>
</tr>
<tr>
<td>[Cu(ptatsc)_2)(NO_3)_2</td>
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<td>90</td>
<td>18</td>
<td>10.79 (10.99)</td>
</tr>
<tr>
<td>[Cu (pvsc)_2 (SO_4)]</td>
<td>Heena Green</td>
<td>85</td>
<td>20</td>
<td>10.89 (10.99)</td>
</tr>
<tr>
<td>[Cu (pvsc)_2 (SO_4)]</td>
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<td>90</td>
<td>18</td>
<td>10.35 (10.41)</td>
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<td>17</td>
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<td>[Cu (ptatsc)_2(SO_4)]</td>
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<td>60</td>
<td>20</td>
<td>11.65 (11.55)</td>
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<td>95</td>
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<td>110</td>
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<td>85</td>
<td>10.79 (10.99)</td>
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<td>$v_1$ (cm$^{-1}$)</td>
<td>$v_2$ (cm$^{-1}$)</td>
<td>$\mu_{\text{eff}}$</td>
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<td>------------------</td>
<td>------------------</td>
<td></td>
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<tr>
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<td>15432</td>
<td>16330</td>
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<tr>
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<td>16341</td>
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<tr>
<td>[Cu(ptasc)$_2$ Cl$_2$]</td>
<td>15400</td>
<td>16241</td>
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<tr>
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<td>16067</td>
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<tr>
<td>[Cu(pvsc)$_2$(NO$_3$)$_2$]</td>
<td>14044</td>
<td>16421</td>
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<tr>
<td>[Cu(pvsc)$_2$(NO$_3$)$_2$]</td>
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<td>16500</td>
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<tr>
<td>[Cu(ptasc)$_2$(NO$_3$)$_2$]</td>
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<td>16168</td>
<td>1.96</td>
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<tr>
<td>[Cu(ptatsc)$_2$(NO$_3$)$_2$]</td>
<td>10256</td>
<td>13200</td>
<td>1.97</td>
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<tr>
<td>[Cu(pvsc)$_2$(SO$_4$)$_2$]</td>
<td>13605</td>
<td>16168</td>
<td>1.96</td>
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</tr>
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<td>[Cu(pvsc)$_2$(SO$_4$)$_2$]</td>
<td>13602</td>
<td>16021</td>
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<td>[Cu(ptatsc)$_2$(SO$_4$)$_2$]</td>
<td>14778</td>
<td>16471</td>
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<td>[Cu(pvsc)$_2$CH$_3$COO)] (CH$_3$COO)</td>
<td>14000</td>
<td>16533</td>
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<td>[Cu(pvsc)$_2$CH$_3$COO)] (CH$_3$COO)</td>
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<td>16520</td>
<td>1.99</td>
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<td>16220</td>
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<td>[Cu(pvsc)$_2$CH$_3$COO)] (CH$_3$COO)</td>
<td>13966</td>
<td>16600</td>
<td>1.99</td>
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**TABLE-3**

**EPR SPECTRAL DATA OF COPPER (II) COMPLEXES:**

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<tr>
<th>Complexes</th>
<th>$g_{ll}$</th>
<th>$g_{ll}$</th>
<th>$g_{iso}$</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(pvsc)$_2$ Cl$_2$]</td>
<td>2.14</td>
<td>2.07</td>
<td>-</td>
<td>2.093</td>
</tr>
<tr>
<td>[ Cu (pvtsc)$_2$ Cl$_2$]</td>
<td>2.10</td>
<td>2.05</td>
<td></td>
<td>2.066</td>
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<tr>
<td>[ Cu (ptasc)$_2$ Cl$_2$]</td>
<td>2.25</td>
<td>2.15</td>
<td></td>
<td>2.183</td>
</tr>
<tr>
<td>[ Cu (ptatsc)$_2$ Cl$_2$]</td>
<td>2.23</td>
<td>2.13</td>
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<td>2.163</td>
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<tr>
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<td>2.19</td>
<td>2.07</td>
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<td>2.110</td>
</tr>
<tr>
<td><a href="NO$_3$"> Cu (pvtsc)$_2$</a>$_2$</td>
<td>2.18</td>
<td>2.06</td>
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<td>2.100</td>
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<tr>
<td><a href="NO$_3$"> Cu (ptasc)$_2$</a>$_2$</td>
<td>2.12</td>
<td>2.05</td>
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<td>2.073</td>
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<tr>
<td><a href="NO$_3$"> Cu (ptatsc)$_2$</a>$_2$</td>
<td>2.11</td>
<td>2.02</td>
<td></td>
<td>2.050</td>
</tr>
<tr>
<td>[Cu(pvsc)$_2$(CH$_3$COO)]</td>
<td>2.19</td>
<td>2.07</td>
<td></td>
<td>2.110</td>
</tr>
<tr>
<td>(CH$_3$COO)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>2.07</td>
<td></td>
<td>2.113</td>
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<td>(CH$_3$COO)</td>
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<tr>
<td>[Cu(ptasc)$_2$(CH$_3$COO)]</td>
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<td>2.04</td>
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<td>(CH$_3$COO)</td>
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<td></td>
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<tr>
<td>[Cu(ptatsc)$_2$(CH$_3$COO)]</td>
<td>2.15</td>
<td>2.06</td>
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TABLE 3

EPR SPECTRA OF SULPHATO COMPLEXES:

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<tr>
<th>Complexes</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$g_3$</th>
<th>R</th>
</tr>
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<tr>
<td>[Cu(pvsc)$_2$ SO$_4$]</td>
<td>1.92</td>
<td>2.042</td>
<td>2.160</td>
<td>.95</td>
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<td>2.020</td>
<td>2.042</td>
<td>2.219</td>
<td>.42</td>
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<td>2.030</td>
<td>2.213</td>
<td>.06</td>
</tr>
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<td>2.034</td>
<td>2.012</td>
<td>2.130</td>
<td>.186</td>
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</tbody>
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