CHAPTER 2

LITERATURE REVIEW

Cuprous iodide (CuI) crystals are grown by slow evaporation technique in three different solvents. Large CuI single crystals with dimensions of 7.5 mm × 5 mm × 3 mm are obtained in pure acetonitrile solvent at 40 °C. The as-grown crystals are analyzed by X-ray diffraction, energy-dispersive X-ray analysis, differential scanning calorimetry, current–voltage characteristic and photoluminescence spectrum. The results show that the CuI crystal has the zinc-blende structure with no secondary phase. The elemental Cu/I ratio is 1.09:1. The melting point of the crystal is 875 K and two phase transitions occur from room temperature to its melting point. The electrical conductivity of CuI platelet crystal is in the range of 1.11–2.38 Ω⁻¹ cm⁻¹. Under ultraviolet excitation, the CuI crystals exhibit three emission bands with peak positions at 426, 529 and 671 nm. The nature of the luminescence is discussed[1]. Neutral tetradentate N2O2 type complexes of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) have been synthesised using a Schiff base formed by the condensation of o-phenylenediamine with acetoacetanilide in alcohol medium. All the complexes were characterised on the basis of their microanalytical data, molar conductance, magnetic susceptibility, IR, UV–Vis 1H NMR and ESR spectra. IR and UV–Vis spectral data suggest that all the complexes are square-planar except the Mn(II) and VO(II) chelates, which are of octahedral and square pyramidal geometry respectively. The monomeric and neutral nature of the complexes was confirmed by their magnetic susceptibility data and low conductance values. The ESR spectra of copper and vanadyl complexes in DMSO solution at 300 K and 77 K were recorded and their salient features are reported[2]. The *in situ* ultraviolet-visible (UV-Vis) spectroelectrochemical study on the copolymerization of diphenylamine (DPA) and o-phenylenediamine (OPD) has been performed at a constant potential of 0.8 V using indium tin oxide (ITO)-coated glass electrodes as working electrode. And also, as a comparison, the electrochemical homopolymerizations of DPA and...
OPD have been investigated by using the in situ spectroelectrochemical technique. The intermediate species generated during the electrochemical homopoly-merization of DPA and OPD, and the copolymerization of DPA with OPD have been identified by using the in situ spectroelectrochemical procedure. The results reveal the formation of an intermediate in the initial stage of copolymerization through the cross-reaction of the cation radicals of DPA and OPD, and the absorption peak located at 538 nm in the UV–Vis spectra is assigned to this intermediate. To further investigate the copolymerization of DPA with OPD, cyclic voltammetry (CV) has been used to study the electrochemical homopolymerization of DPA and OPD and also the copolymerization of DPA and OPD with different concentration ratios in solution. The different voltammetric characteristics between the homopolymerization and copolymerization processes exhibit the occurrence of the copolymerization, and the difference between the copolymerization of DPA and OPD with different concentration ratios shows the dependence of the copoly-merization on the concentrations of DPA and OPD. The copolymer has also been characterized by Fourier transform infrared spectroscopy (FT-IR)[3].

A detailed correlation is presented between the in situ Fourier transform-infrared (FT-IR) spectra of adsorbed CO2, CuBzPyz host bands, and CO2 adsorption sites using previously reported crystal structures of CO2-loaded CuBzPyz and CO2 adsorption isotherms. Through the analysis of both in situ attenuated total reflectance FT-IR spectra taken at several points on the high pressure isotherm and in situ transmission FT-IR spectra acquired at low pressures and cryogenic temperatures, we provide additional insight into the pore-filling mechanism of CO2 on the structurally dynamic CuBzPyz host. The FT-IR spectrum of adsorbed CO2 shows distinct ν2 and ν3 spectral features that can be attributed to known CO2 adsorption sites observed in the reported crystal structure of the CO2-saturated phase of CuBzPyz. The availability of detailed high quality CO2-loaded structural data for CuBzPyz makes this system a case study for associating infrared spectral features with CO2
adsorption sites and should prove valuable for future interpretations of CO2 host–guest and guest–guest interactions when X-ray quality structural data is unavailable\[4\]. Four copper(II) α,β-unsaturated carboxylate complexes with imidazole, Cu(CH$_2$=CH–COO)$_2$(imH)$_2$ (1), Cu$_2$(CH$_2$=CH–COO)$_4$(imH)$_2$ (2), Cu[CH$_2$=C(CH$_3$–COO)]$_2$(imH)$_2$ (3) and Cu$_2$[CH$_2$=C(CH$_3$–COO)]$_4$(imH)$_2$ (4) (where imH=imidazole) have been prepared and characterized by elemental analyses, IR, ESR and electronic reflectance spectroscopies. The single crystal X-ray diffraction study of complex 3 shows that the copper(II) atom is in a symmetric centre of a square planar environment completed by two monodentate α-methacrylate groups and two imidazole ligands displayed in trans position. Each molecular unit is linked with four neighbouring units by hydrogen-bond interactions forming a two-dimensional supramolecular compound (d$_{N···O}$=2.781 Å). Complex 1 has a similar structure as complex 3, while complexes 2 and 4 have a binuclear cage structure. The ESR spectra show that the spin coupling between the unpaired electrons of Cu(II) atoms present in complexes 2 and 4, is not observed in complexes 1 and 3. The electronic reflectance spectra suggest that the d–d transitions of complexes 1 and 3 are in a square planar ligand field, while that of complexes 2 and 4 are in a tetragonal ligand field, and the ligand field strength of acrylate group and α-methacrylate group is similar. Complexes 1 and 2 as well as 3 and 4, were produced simultaneously in the reaction of the corresponding copper(II) α,β-unsaturated carboxylate with imidazole in methanol solution\[5\]. The electronic absorption spectra of spherocrystals of Ni(IO$_3$)$_2$ · 2 H$_2$O, Mn(IO$_3$)$_2$ and 3 Cu(IO$_3$)$_2$ · 2 H$_2$O were measured. Some new absorption peaks were obtained. Measured energy splitting by low-symmetric crystal field and spin-forbidden transitions are clearer than the results of diffuse reflection spectrum. And the experimental results were interpreted theoretically by means of nonfree radial wave functions and ligand field theory. The experimental results and the calculated values coincide\[6\].
P. Balaya describes briefly the experimental facilities developed for the measurement of thermal conductivity of solids in the temperature range 10K–300K. Different techniques have been used for the determination of thermal conductivity, depending on the relaxation time of the system under investigation. Measurements on stainless steel 304, using steady state and non-steady state methods are presented. Values of thermal conductivity obtained by both these methods agree to each other and are consistent with those reported earlier[7]. Ya. A. Landa was studies that The advantages of the hot-wire method of determining the thermal conductivity of refractory products lie in the fact that it makes it possible to determine the true thermal conductivity directly in relation to a given temperature of the specimen. This fact distinguishes this method favorably from the methods based on the use of tablets and cylinders in which the thermal conductivity is related to the mean temperatures of the hot and cold sides on the specimen. The hot-wire method gives satisfactory results even when λ is low, i.e., 0.05–0.18 W/m·deg K [in the standard method (GOST 12170-76) the lower limit in the determination of the thermal conductivity of refractories is 0.18 W/m·deg K]. The method is convenient for determining the thermal conductivity of refractories in granular and powder form. Among the disadvantages of the method are the fact that it cannot be used to determine the thermal conductivity of anisotropic materials, the complexity of the measuring process and the high degree of skill demanded from the operator, and the long duration of the measuring process at a given temperature. The investigations on the experimental device developed at the All-Union Institute of Refractories demonstrated that the hot-wire method can be used for refractories with a low or moderate thermal conductivity[8]. The cobalt(II), cadmium(II), copper(II), mercury(II), nickel(II) and zinc(II) complexes of diethyldithiocarbamic acid were prepared and investigated by TG, DSC thin-layer chromatography and gas-liquid chromatography. Heats of fusion were determined[9]. The preparation of chalcone ligand and complexes of zinc, cadmium, mercury with chalcone is described. Thermogravimetric
measurements made on these samples show ligand to be more stable than the metal complexes as it exhibits higher initial decomposition temperature by J. Meena Devi and supporter. Thermal diffusivity of these four samples is measured by photoacoustic technique at room temperature to find the influence of coordination of metal on the thermal properties of chalcones. Experimental results indicate that the thermal diffusivity of chalcone metal complexes is enhanced when compared to the parent ligand. If we consider the free electron density of metals, then the increase may be understood from the electronic contribution of metals to the thermal property. So among metal complexes, thermal diffusivity increase with the increase in the free electron density of the metal ion coordinated\(^{[10]}\).

Synthesis, structural, thermal and biological studies of Cr(III), Mn(III), Fe(III), Vo(IV), Th(IV), Zr(IV) and UO\(_2\)(VI) Schiff base complexes have been carried out by Mandlik\(^{[11]}\). Reddy and his coworkers reported synthesis, spectral and antimicrobial studies of transition metal with amide derivatives of 2-amino pyridine\(^{[12]}\). Schiff base ligands coordinate to many metals in various oxidation state and have attracted much attention. By modifying the structures of schiff bases, many well-designed Schiff base ligands have been prepared, for instance, macrocycle Schiff base, pyridine containing dicarbonyl ligands, chiral Schiff bases, and so on. Large number of researchers have indicated that complexes with schiff base ligands have biological activity\(^{[13]}\). Complexes of some divalent metal ions with Schiff base derived from salicylaldehyde and tyrosine have been prepared and investigated by using different physical tools and an octahedral structure was proposed for all complexes\(^{[14]}\). Synthesis of Co(II), Cu(II), Ni(II) and Zn(II) complexes with thiazole ring containing Schiff base ligands and their antimicrobial activities were tested against eight different microorganisms\(^{[15]}\). Cobalt(II), Copper(II), Nickel(II) and Zinc(II) complexes of two novel Schiff base ligands and their antimicrobial activity has been studied\(^{[16]}\). J. T. Makode and colleagues measured Polychelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and VO(IV) with a new bis-
chelating Schiff base derived from 5-acetyl-2,4-dihydroxyacetophenone and isonicotinic acidhydrazide have been synthesized. The resulting polychelates have been characterized by elemental analyses, IR and electronic spectral data, magnetic susceptibility measurements and thermogravimetric analysis. All the polychelates are dark coloured solids and insoluble in water and common organic solvents. Thermogravimetric analyses confirm coordination of water in complexes. Various kinetic and thermodynamic parameters have been evaluated from thermal data. The ligand acts as a bis-tridentate molecule coordinating through deprotonated phenolic/enolic oxygen atoms and azomethine nitrogen atoms. The solid-state conductivity of ligand and its polychelates have been measured in their compressed pellet form and all compounds were found to be semiconducting in nature\textsuperscript{[17]}. Mixtures of CuCl\textsubscript{2} and KCl with molar ratios of Cu to K from 0.5 to 1.0 were heated at 393 K and then they absorbed water from the surroundings at room temperature. DTA, TG and DTG curves were analyzed for the mixtures with absorbed water in the temperature range between 293 and 473 K. The mechanism of the phase changes and water release from the mixtures in the temperature range from 293 to 473 K is proposed\textsuperscript{[18]}. Attempts to prepare heterobimetallic complexes in which 3d and uranium magnetic ions are associated by means of the Schiff bases H(2)L(i) derived from 2-hydroxybenzaldehyde or 2-hydroxy-3-methoxybenzaldehyde were unsuccessful because of ligand transfer reactions between [ML(i)] (M=Co, Ni, Cu) and UCl(4) that led to the mononuclear Schiff base complexes of uranium [UL(i)Cl(2)]. The crystal structure of [UL(3)Cl(2)(py)(2)] [L(3)=N,N'-bis(3-methoxysalicylidene)-ethylenediamine; py=pyridine] was determined. The hexadentate Schiff base ligand N,N'-bis(3-hydroxysalicylidene)-2,2-dimethyl-1,3-propanediamine (L) was useful for the synthesis of novel trinuclear complexes of the general formula [[ML(py)](2)U] (M=Co, Ni, Zn) or [[CuL(py)]M'[CuL]] (M'=U, Th, Zr) by reaction of [M(H(2)L)] with [M'(acac)(4)] (acac=MeCOCHCOMe). The crystal structures of the Co(2)U, Ni(2)U, Zn(2)U, Cu(2)U, and Cu(2)Th complexes show that the
two ML fragments are orthogonal, being linked to the central actinide ion by the two pairs of oxygen atoms of the Schiff base ligand. In each compound, the UO(8) core exhibits the same dodecahedral geometry, and the three metals are linear. The magnetic study indicated that the two Cu(2+) ions are not coupled in the Cu(2)Zr and Cu(2)Th compounds. The magnetic behavior of the Co(2)U, Ni(2)U, and Cu(2)U complexes was compared with that of the Zn(2)U derivative, in which the paramagnetic 3d ion was replaced with the diamagnetic Zn(2+) ion. A weak antiferromagnetic coupling was observed between the Ni(2+) and the U(4+) ions, while a ferromagnetic interaction was revealed between the Cu(2+) and U(4+) ions[19].
REFERENCES


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