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Synthesis and characterization of a new variety of Cu(II) and Fe(II) metal complexes, including chloranilic acid

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ABSTRACT

One dimensional polymer of the types $M_xM^1_{1-x}(CA)$(where, M-Cu(II),M^1=Fe(II), CA (chloranilic acid) = 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone and (X= 0;0.25;0.50;0.75 and 1) have been synthesized and characterized by elemental analyses, magnetic susceptibility, IR, UV-visible, and X-ray powder diffractional studies. The powder XRD studies confirm the complexes are crystalline in nature having monoclinic crystal geometry. The solid state variable temperature electrical conductance measurement exhibits semiconductor behavior. The entire compounds exhibit compressed pellet room temperature conductivity in the 9.23×10^{-8} to X 3.76×10^{-7} S/cm, respectively.   © 2009 Trade Science Inc. - INDIA

INTRODUCTION

One of the major interests in coordination chemistry is to study the interaction of a central atom with surrounding atoms, ions or molecules. Coordination compounds containing chloranilic acid {H_2CA (3, 6-dichloro-2, 5-dihydroxy-1, 4-benzoquione)} have been known and studied in the beginning of this century, and also belongs, are interesting systems from the point of view of electrontransfer reactions, which play an important role in biological systems.[1-4] and are among the most pervasive natural products on the earth's surface and also found in most living organisms.[5] Inorganic semiconducting complexes constitute one of the most fascinating, recent research topics, deeply involving both chemists and solid states physicists. While some of the initial impetus for such research has no doubt been stimulated by the progress that has been achieved from the study of the solid state properties of inorganic materials. The theoretical and practical consequences of studies of the organic solid state cannot as yet be clearly as certained, and they may not necessarily follow the route set by the inorganic solid state.[6] Semiconducting organic solid materials are frequently grouped into the categories of molecular crystals, charge transfer complexes, and polymers. Inorganic semiconductors stand on the threshold of a bright and exciting future. An organic semiconductor can be synthesized with properties comparable to those exhibited by inorganic semiconductor materials such as development for transistors and the wide array of now-existing derivative devices and components of the electronics industry. The purpose of this study is to investigate the metal-chloranilate system toward new type of materials. The routine structure determination from single-crystal X-ray diffraction (XRD) is one of the principal triumphs of

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crystallography. However, many crystalline solids can be obtained only as microcrystalline powders, and they are not suitable for investigation by single-crystal diffraction methods. There is clearly a pressing need to exploit techniques for solving crystal structures from powder diffraction data. Powder XRD has been used routinely as a fingerprinting technique for decades, and it has also been used in studies related to polymorph identification and to calculate unit cell parameters. Despite the loss of information, which is due to peak overlap, a high quality powder diffraction pattern often contains enough information for unambiguously determining the corresponding crystal structure. In fact, there has been a rapid development of techniques for structure determination from powder diffraction data.[7-11]

Our recent studies devoted to the synthesis and characterization of new metal chloranilate assemblies. As a part of our research on metal chloranilate intercalation chemistry, we have synthesized a series of common intercalation compound and observed it temperature dependent electrical properties and crystal structures respectively.

2. EXPERIMENTAL

The Electronic absorption spectra were recorded in solid state in Nujol Mull,[12] on a UV-1700 Pharmaspec. UV-visible spectrophotometers. Infrared (4000-400 cm^{-1}) spectra were recorded on a Varian 3100 FT-IR Excalibur Series, sample were prepared using the KBr disc method. Elemental analysis measurements of the complexes were recoded on a Model CE-440 CHN analyzer. Magnetic susceptibility of the powder samples measured on a Cahn, Faraday electrobalance using CoHg (SCN)$_4$ as calibrant. X-ray powder diffraction (XRD) patterns of the complexes were recorded on a X-ray diffractometer (Seifert, D-2070) using Cu Kα as the radiation source ($\lambda = 1.5418$ Å). Pressed pellet electrical conductivities of the complexes were measured over a 300-348 K temperature range using conventional two probe technique on a keithley 3330 LCZ meter source measure unit. The pellets were made at a pressure of 7 ton and electrical contacts of the pellet surfaces were made using silver paint.

Preparation of complexes

The copper chloranilate CuCA and FeCA complexes were prepared according to the literature procedure.[13]

A solution of 1362.06mg (10mmol) of $CH_3COONa.3H_2O$ in 20cm^3 water was added to a solution of 208.9mg (1mmol) of chloranilic acid and 112.1mg (2mmol) of KOH in 20cm^3 DMF. Then a molar ratio of $FeSO_4.7H_2O$ and $CuCl_2.2H_2O$ (both were dissolved in 50% v/v water and DMF (10ml) were added above solution, dark green colour precipitated solution was additionally stirred 6hrs, and then filtered. Washed several time with water and finally ethanol and dry under desiccator over $CaCl_2$. Yield of all complexes are about (70-80%) and their colour are very minute differences between them. All complexes are prepared in same manners, differences only the molar ratio of metal ion.

3. RESULTS AND DISCUSSION

All the complexes were formed as fine powders. These solids decomposes in the temperature range 200-250ºC. The compounds were characterized by IR, magnetic susceptibility, UV-visible, Powder X-ray diffractional and pressed pellet conductivity technique. The compounds are insoluble in water as well as common organic solvents such as ethanol, methanol, acetonirile and dichloromethane but slightly soluble in highly polar solvents like DMF and DMSO.

3.1. IR spectra studies

The I.R spectral bands of the complexes are summarized in TABLE 1.

The IR spectra of all the complexes seem to be approximately similar in their vibrational frequencies. Here we will only discuss the selected infrared bands.

TABLE.1 : Comparison the Infra red spectral data sheet with ligand and its mono and bimetallic complexes

S.No	Compound	C=C Str. C–O Str.	C–O Str. C–C Str.	-C–C-Str.
1.	CA	1630s	1369s	1266s
2.	FeCA	1494s	1377s	1302w
3.	Fe0.75Cu0.25CA	1499s	1378s	1313w
4.	Fe0.50Cu0.50CA	1491s	1368s	1309w
5.	Fe0.25Cu0.75CA	1484s	1365s	1306w
6.	CuCA	1489s	1370s	1318w

m medium, s = strong, w = weak

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The characteristic absorptions present in the infrared spectra of the free ligand, H_2CA, arising from the ν(C-O), and ν(C-C), modes appear at 1664 and 1630 cm^{-1} respectively,[14] which is shifted to lower frequency region in the complexes indicating the participation of CA group in chelation. Only two C-0 stretching bands are observed in the IR spectra at ~1484-1499cm^{-1} and 1365- 1378 cm^{-1}. This agrees with D_2h symmetry for the CA ligand and suggests a bridging bis-bidentate coordination mode of the complexes[15]. In general, lattice water absorbs at 3550-3200 cm^{-1} for both the antisymmetic and symmetic OH stretching and at 1630-1600 cm^{-1} (HOH bending)[16]. In all complexes a broad absorption band at ca. 3400 cm^{-1} and the absorption at 1620 cm^{-1} indicate the presence of lattice water.

3.2. Electronic spectra and magnetic susceptibility studies

The electronic absorption bands are displayed in Figure 1. Elemental analyses, IR, electronic spectra and magnetic susceptibility measurements have indicated that the reaction of MCl_2 and $MSO_4.XH_2O$ (M= Cu, Fe and X= 2, 7) with chloranilic acid yields the complexes CuFe $(CA)_2.nH_2O$.

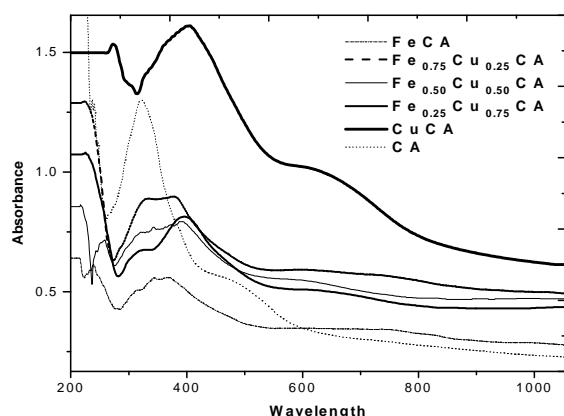**Figure 1 : Electronic absorption spectra of the complexes in nujol mulls**

A broad band at about 17000 - 19000 cm^{-1} was observed in the electronic spectra of all complexes. It is attributed to charge transfer bands arising from chloranilic acid ligands, as expected for P-benzoquinone[17], supporting also a bridging bis-bidentate coordination proposed for chloranilic acid.

In ironchloranilate, iron (II) ion has magnetic moment of 4.93 B.M expected for d[6]- system in a high spin octahedral configuration[18]. Whereas the μ_{eff} value of $Fe_{0.5}Cu_{0.5}CA$ complex in comparison to its monomer units are lower than some of the magnetic moments contributed by Fe^{2+} 3d[6] or Cu^{2+} 3d[9] paramagnetic centers showing some short of antiferromagnetic interaction between (Fe-Cu or Cu-Cu) in these species.

3.3. X-ray diffraction characterization

Figure 2 shows the XRD powder patterns of the some compound recorded between 2 θ =10 to 80[0] and the observed diffraction data, i.e. d values, relative intensities, and 2θ of the compounds, are given in TABLES 2. This figure demonstrates that the compound is a crystalline phase having the monoclinic crystal geometry.

TABLE.2 : Observed and calculated powder X-ray diffraction data of the complexes

S.N0.	2 θ	Intensity	d	Q(obs.)	Q(calc.)	h k l
CuCA S= ~33nm						
1.	17.844	283	4.967	0.0405	0.0382	-210
2.	23.566	282	3.772	0.0703	0.0708	-211
3.	28.526	1000	3.126	0.1023	0.1054	002
4.	34.192	203	2.620	0.1457	0.1459	120
5.	40.810	198	2.209	0.2049	0.2066	-411
6.	48.281	151	1.883	0.2819	0.2831	-422
7.	63.142	166	1.471	0.4620	0.4583	123
FeCA S = ~ 40.99nm						
1.	13.984	931	6.328	0.0249	0.0254	001
2.	22.118	648	4.016	0.0620	0.0589	011
3.	25.028	421	3.555	0.0791	0.0726	-211
4.	26.481	375	3.363	0.0884	0.0897	-210
5.	28.438	1000	3.136	0.1017	0.1016	002
6.	31.207	388	2.864	0.1219	0.1216	-311
7.	32.852	358	2.724	0.1348	0.1352	012
8.	43.288	346	2.088	0.2293	0.2347	-322
9.	49.008	483	1.857	0.2899	0.2905	-422
10.	49.771	340	1.830	0.2985	0.2993	-421
Fe_{0.75}Cu_{0.25}CA S = ~ 58.23nm						
1.	14.013	1000	6.315	0.0251	0.0256	001
2.	22.017	428	4.034	0.0615	0.0574	011
3.	28.376	548	3.143	0.1013	0.1023	002
4.	31.541	561	2.834	0.1245	0.1241	-311
5.	33.477	251	2.675	0.1398	0.1422	120
6.	51.881	261	1.761	0.3225	0.3227	-414
Fe_{0.5}Cu_{0.5}CA S = ~ 28.87 nm						
1.	14.340	467	6.1714	0.0263	0.0241	001
2.	27.389	1000	3.2536	0.0945	0.0965	002
3.	31.541	20	2.8341	0.1245	0.1242	-311
4.	40.810	80	2.2093	0.2049	0.2051	-411
5.	43.288	94	2.0884	0.2293	0.2294	-322
6.	59.165	65	1.5603	0.4108	0.4107	-521

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Values of the unit cell parameters a, b and c were found by using a computer based d h k l analysis program was used to compute the cell parameters.

These values of the cell parameter are very close to those reported for Chloranilic acid in JCPDS ASTM files 22-1610. The crystalline size(S), as estimated using the Scherrer formula[19], are also given in TABLES 2. The most intense(1000) diffraction peak was used for determination of the crystalline size. The complex CuCA is monoclinic with the unit cell parameters a = 10.2453 A°, b=5.5383 A°, c = 7.8582 A°, β = 128.372⁰, and cell volume V=349.5742 A°. The FeCA complex is monoclinic with the cell parameters a = 10.2036A°, b=5.4617 A°, c = 7.5870 A°, β = 124.2268⁰, and cell volume V=334.1624 A°, respectively whereas that for $Fe_{0.75}CACu_{0.25}$ and $Fe_{0.5}CACu_{0.5}$ complexes are also monoclinic with the cell parameters a = 10.003A°, b= 5.6039A°, c = 7.6142A°, β = 124.8053 ⁰, with cell volume V= 350.4635 A°, and a = 9.9894A°, b= 5.6040A°, c = 7.7594A°, β = 123.9062⁰, with cell volume V= 360.5104A° respectively.
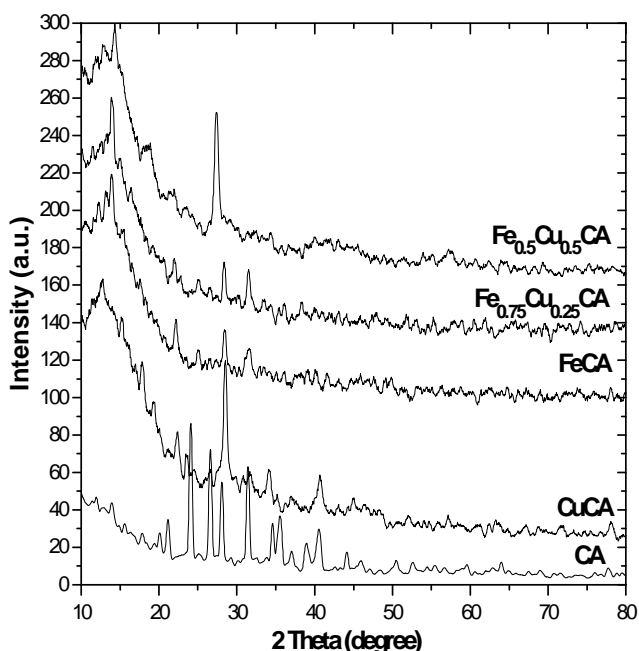

Figure 2 : Comparison of the X-ray powder diffraction patterns of the following complexes

3.4. Electrical conductivity

Room temperature electrical conductivity, (displayed in Figure 3) capacitance, dielectric constant and

their activation energy are summarized in TABLE 3.

In Figure 3, temperature dependence of the conductivity semiconductor materials is examined according to Arrhenius theory. Arrhenius plot of conductivity versus temperature is shown according to following:

$$\sigma = \sigma o \exp(-Ea/KT) \tag{1}$$

Where, σo is the pre-exponential corresponding to 1/T=0, Ea is the activation energy for electron transfer, and k is the Boltzmann constant. These results allowed the following observations.

(a) As seen in Figure 3, these complexes, at temperature range between 300–328 K, behave as have semiconducting when the conductivity increases with temperature. Thus, a plot of log σ and 1000/T will be a straight line of slope -Ea/kT and hence an accurate determination of Ea is possible if we can find slope of log σ vs. 1000/T curve. The activation energies of these samples are calculated from the slope of graphs and these values are collected in TABLE 3.
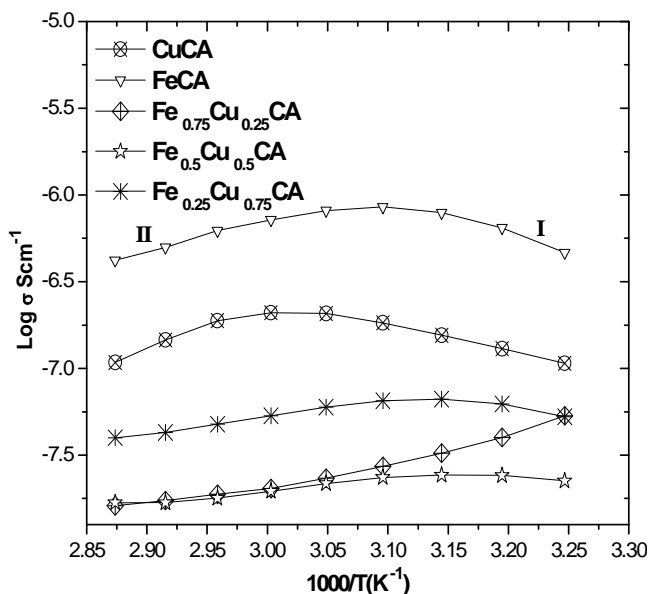

Figure 3 : Temperature dependence of the electrical conductivities of the complexes

(b) The curves of samples explain a positive temperature coefficient of conductivity with conventional semiconducting behavior when the conductivity increases with increase temperature and so, these plots indicate typical plots semiconductor. Temperature dependence of the conductivity curve of all sample exhibits two regions; I, II as

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seen in Figure 3. I region has a positive temperature coefficient of electrical conductivity, but region II has a negative value. Therefore, the electrical activation energy of this sample explains positive value in the region I, but negative in II. The region II is characterized by decrease of the conductivity with temperature. This results from scattering of carriers by photons, due to lattice vibrations within the temperature range covering this part. The slope of line II and its temperature range vary widely depending on the nature and structure of the sample. The phenomena of discontinuation observed in the electrical conductivity–temperature relationship showed one or two segments with variable activation energies, probably due to presence of different crystallographic or phase transition[20].

(c) Electrical conductivity mechanism of these complexes occurs as follows; in this mechanism, the electron or hole hops from one localized metal site to the next. When it lands on a new site it causes the surrounding ions to adjust their localization and electron or hole trapped temporarily in the potential well this atomic polarization produces. The electron resides at its new site until thermally activated to migrate another nearby site. Another aspect of this charge hopping mechanism is that the electron or hole tends to associate with local defects so the activation energy for charge transport may also include the energy of freeing the hole from its position next to defect[21,22].

(d) Thermal probe measurements show that these complexes have n-type electrical conductivity, that is, most of carriers into samples are electrons.

(e) As the conductivities of complexes were compared with each other, it was found that the conductivity of FeCA complex was higher and $Fe_{0.5}Cu_{0.5}CA$ complex was lower than that of other complex (see inset of Figure 3). In one complex $Fe_{0.75}Cu_{0.25}CA$ are almost insulating behavior.

The capacitance of the sample was measured by varying the frequency. The dielectric constant (ε) in the frequency range of 40 Hz–100 kHz was estimated by using the formula $\varepsilon = C/(\varepsilon o.A/l)$, where C is the capacitance of the pellet, l is the thickness of the pellet, A is the cross-sectional area and εo the constant of permittivity of free space. Figure 5 shows the dielectric constant increase with increase the temperature.
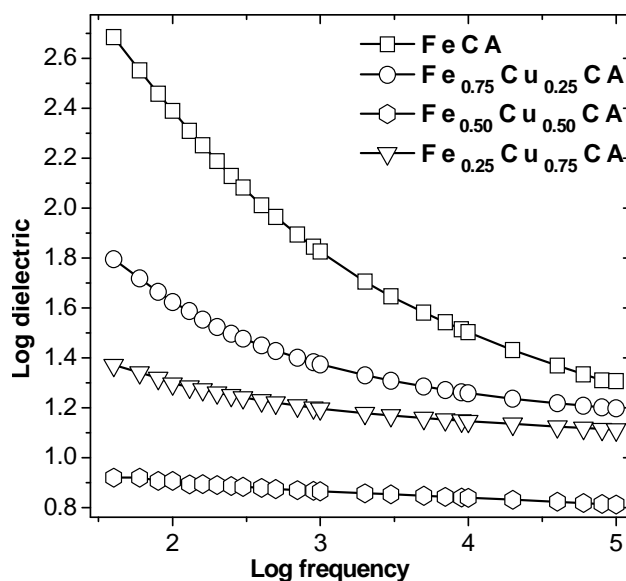

Figure 4 : Frequency dependence of dielectric constant for various complexes

In general the dielectric constant of a material depends on its polarizability which is made up of several components; electronic, atomic, orientational and space charge. Of these, only the orientational polarization (i.e., the contribution of the permanent dipoles in the material) is directly temperature dependent.

The temperature dependence of the dielectric constant (ε) of a dielectric material is very critical for dielectric resonator applications. In the present study, the temperature variation of dielectric constant of all the samples are accurately measured in the 25–75 °C region and the results are presented in Figure 5. All the samples in all frequencies (100Hz; 1KHz; 10KHz and 100KHz) shows an increase in dielectric constant with respect to temperature and then decrease at a particular temperature. In all cases, both frequencies show similar variation in capacitance with respect to temperature. Hence, the comparisons in capacitance observed at 100Hz to 100 KHz are presented in the Figure 5.

It can be seen in the Figure 5 that all complexes have both the positive and negative temperature coefficient.
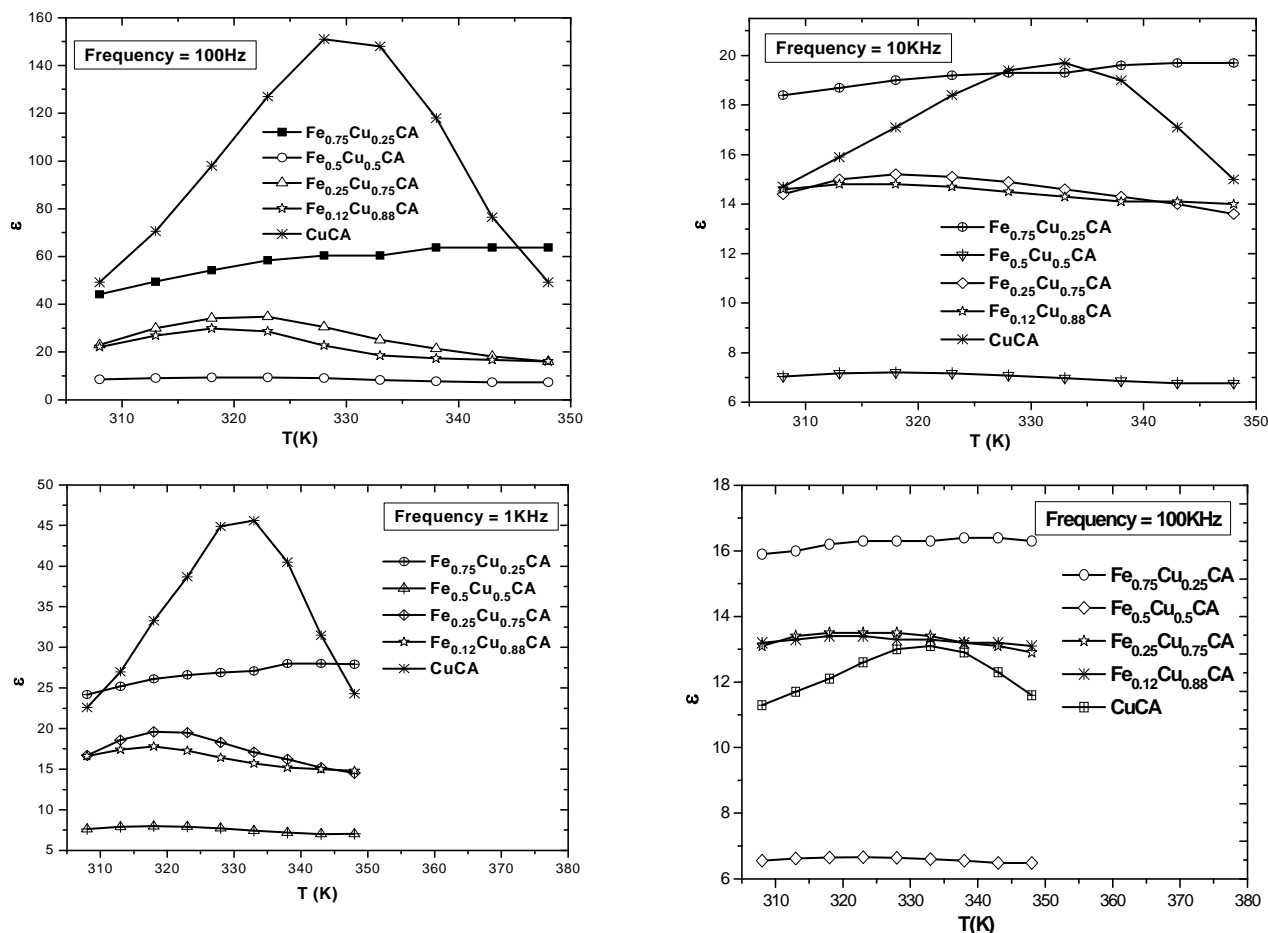
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Figure 5 : Temperature verses Dielectric of various complexes at 100Hz, 1 KHz, 10 KHz and 100 KHz frequencies

TABLE 3 : Room temperature (100 KHz) frequency electrical conductivity, capacitance, dielectric constant and their Activation energies

Compound	Electrical conductance $G(\mu s)$ Scm^{-1}	Electrical conductiviy $\sigma = Gl/A$	Log Scm^{-1}	Capacitance $P(F)$	$\varepsilon = C/Co$	Ea_1 in eV	Ea_2 in eV
FeCA	5.38×10^{-6}	3.76×10^{-7}	6.424	2.57×10^{-11}	20.3	0.46	0.32
Fe0.75	1.52×10^{-6}	9.11×10^{-8}	7.041	2.32×10^{-11}	15.8	-	0.14
Fe0.50	0.94×10^{-6}	2.10×10^{-8}	7.677	2.58×10^{-11}	6.50	-	0.16
Fe0.25	1.03×10^{-6}	4.88×10^{-8}	7.311	2.42×10^{-11}	13.0	0.19	0.20
CuCA	2.48×10^{-6}	9.23×10^{-8}	7.035	2.60×10^{-11}	10.9	0.30	0.43

(1) A positive curve shows below the 320 – 330K temperature because dielectric constant increases with increases temperature and,

(2) A negative curve shows above the ~ 330 K temperatures because dielectric constant decreases with increases temperature, which suggests the existence of phase change at this temperature. These observations are also support the temperature dependant electrical conductivity of com-

plexes. No other dielectric anomalies were found between these regions.

By comparing figures 100 Hz, 1 KHz, 10 KHz and 100 KHz frequency we find that at high frequency dielectric constant and its temperature coefficient are smaller than at low frequency. In order to further investigate this frequency dependence, Figure 4 shows the cell capacitance versus frequency at room temperature. The change in cell capacitance with frequency is larger

than that observed in the 25°C to 50°C range measured at a given frequency.

4. CONCLUSIONS

The dianions derived from chloranilic acid are effective ligands for the metal studied in this paper. In this work, we have synthesized and characterized a new type of polymer using as bridging ligand the CA^{2-} dianion. Structural studies of samples indicated that all complexes are monoclinic system with different particle size respectively. Also, these complexes have been found to be inorganic semiconductors having moderate conductivities and activation energies.

ACKNOWLEDGMENTS

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