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Synthesis, characterization and electrical behavior of some Chalcones based heterobimetallic complexes of dithioligands

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Abstract

New semiconducting materials with proper band gap range are the demand of the semi-conducting electronic material industry. Several dithio complexes are reported to show good semiconducting properties. The present paper involve synthesis, characterization and study of variable temperature solid-state electrical conductivity of heterobimetallic complexes $[M(CS_3)_2][M'(L)_2(H_2O)_2]$ where [M= Cu(II), Zn(II) and M′= Fe(II), Ni(II), Co(II) and CS_3^{2-} = tri-thiocarbonate, L = Chalcone based ligand . These complexes have been characterized by elemental analysis, FT-IR, ^1H & ^{13}C-NMR, UV-Visible and powder XRD spectra and solid-state electrical conductivity. These complexes show electrical conductivity in a range of $\sigma_{rt} = 2.1\times10^{-5} – 8.8 \times10^{5}$ (Scm^{-1}) .

Keywords: Heterobimetallic, Chalcone, Semiconductor, dithio complexes, Electrical conductivity

1. Introduction

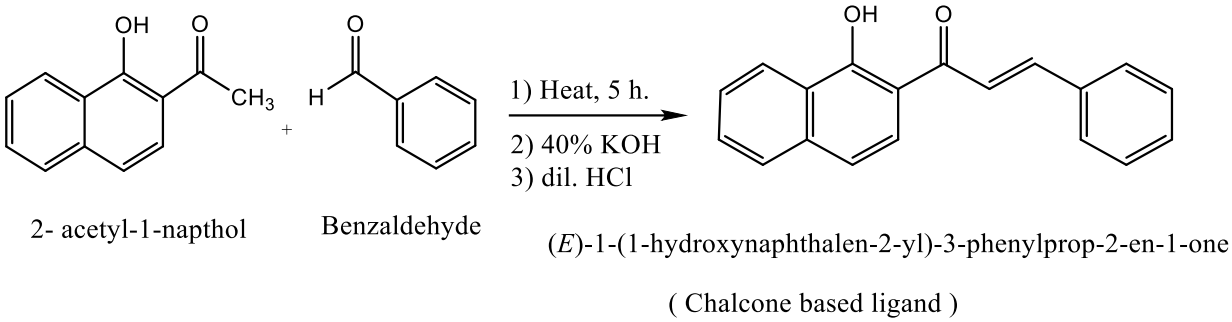
The non-linear optical properties of chalcones such as excellent blue light transmittance and crystallization ability have been reported. They show good optical limiting properties with nanosecond layer pulse at 532 nm wavelength. A Conjugated system with hetero atoms is the interest of chemists for the synthesis of metal-based semiconducting molecular material.[1-9]

Several works have been reported with complex related monometallic complexes having the band in the range of good semiconductors.[9-14] We report here in the synthesis, characterization and solid-state electrical conductivity of some new chalcones based mono, bimetallic complexes of the type$[M(CS_3)_2][M'(L)_2(H_2O)_2]]$ where [M= Cu(II), Zn(II) and M′= Fe(II), Ni(II), Co(II), CS_3^{2-} = tri-thiocarbonate, L = chalcone based ligand. There structure aspects and electrical behavior were analyzed.

2. Experimental

2.1 Preparation of Chalcone based ligand (L) :

Benzaldehyde (0.1 mol) and 2-acetyl-1-naphthol (0.1 mol) were taken in 25 ml ethanol and stirred at room temperature for 1 hour after that 1.5 ml of 40 % KOH solution was added and the reaction mixture was kept at room temperature overnight. Then the reaction mixture was poured into ice-cold water containing dil. HCl. The solid product obtained was filtered off and recrystallized in ethanol and kept over $CaCl_2$.



2- acetyl-1-napthol Benzaldehyde

(*E*)-1-(1-hydroxynaphthalen-2-yl)-3-phenylprop-2-en-1-one

(Chalcone based ligand)

Figure. 1. Preparation of chalcone based ligand (Claisen- Schmidt condensation)

2.2 Preparation of tri-thiocarbonate ligand:

The potassium salt of K_2CS_3 was prepared in situ by adding an aqueous solution of KOH to the solution of carbon disulfide (CS_2) in DMF at 15-20 ^{0}C by literature method.

2.3 Preparation of complexes

The chalcone ligand was complexed with metal salt (Ferrous sulfate/Cobalt Chloride/Nickel Chloride) by usual methods. The metal salts solutions in ethanol-water (1:1, V/V) was slowly added with stirring to the solution of ethanolic chalcone ligand solution, to get the metal chalcone complex. The salts $K_2[Zn(CS_3)_2]$/$K_2[Cu(CS_3)_2]$ was prepared by slow addition of saturated ethanolic-water solution of copper sulfate/Zinc acetate to the solution of a tri-thiocarbonate ligand. The solution of $K_2[Zn(CS_3)_2]$/$K_2[Cu(CS_3)_2]$ thus prepared was filtered into the metal-chalcone complex solution and was stirred for 4-5 hours at room temperature. The resulting products were filtered off and dried under vacuum over $CaCl_2$.

3. Analysis and Physical Measurements

Elemental examinations (C, H and N) were done on a Carlo Erba 1108 component analyzer. Metal and sulfur were determined by gravimetrically standard techniques and the organic part of the complex were disintegrated with conc. HNO_3. The melting point was checked in an open capillary and uncorrected. TLC on silica gel plates was used for purity checking and reaction progress. The UV-Visible spectra were acquired in DMSO-d_6 with UNICAM UV-300 spectrophotometer and FT-IR spectra were recorded on an FT-IR Nicolet 510 spectrometer by the standard KBr disc technique over the range of 500- 4000 cm-1 with a resolution of 4 cm^{-1} and ^{1}H & ^{13}C-NMR spectra were recorded 600 MHz models utilizing DMSO-d_6 as dissolvable. Powder XRD spectra of the complexes were gathered at room temperature on a Seifert model ID-300 and nickel channel (λ= 1.5406 Å). The XRD designs were estimated at 2ɵ in the range of 20˚-90˚. The Bragg's condition was used to find out the interlayer dispersing d by using Bragg's condition $n\lambda = 2d\sin\theta$ where n is the order of reflection and Θ is the angle of reflection. Packed pellet electrical conductivity of the buildings was obtained Schlumberger Impedance/Gain stage assessment model, (Si-1260) and Keithley 236 source measure unit (SMU) by using two test systems. The heap of 20KN was used course of action of round plate shape pellets secured with Eltecks silver paste for electrical contact the block was assessed at a repeat of a 1 kHz. The temperature was controlled inside ± 1 ^{0}C temperature stretch out (on Schlumberger impedance analyzer).

Table .1 Physical Analytical data of the complexes

S. No.	Complexes $[M(CS_3)_2][M'(L)_2(H_2O)_2]$	m.p./d.p (°C)	% C	% H	% S	% M	% M′
1	$[Cu(CS_3)_2][Ni(L)_2(H_2O)_2]$ $C_{40}H_{34}CuNiO_7S_6$	121	51.20 (51.05)	3.33 (3.16)	2.50 (2.56)	6.67 (6.60)	6.26 (6.00)
2	$[Cu(CS_3)_2][Co(L)_2(H_2O)_2]$ $C_{40}H_{34}CuCoO_7S_6$	129	51.19 (51.16)	3.33 (3.21)	2.50 (2.48)	6.77 (6.31)	6.28 (6.04)
3	$[Cu(CS_3)_2][Fe(L)_2(H_2O)_2]$ $C_{40}H_{34}CuFeO_7S_6$	117	51.36 (51.00)	3.34 (3.16)	2.56 (2.32)	6.79 (6.22)	5.97 (6.11)
4	$[Zn(CS_3)_2][Ni(L)_2(H_2O)_2]$ $C_{40}H_{34}ZnNiO_7S_6$	109	51.10 (51.12)	3.32 (3.17)	2.46 (2.19)	6.95 (6.66)	6.24 (5.99)
5	$[Zn(CS_3)_2][Co(L)_2(H_2O)_2]$ $C_{40}H_{34}ZnCoO_7S_6$	124	51.09 (51.06)	3.32 (3.03)	2.46 (2.16)	6.95 (6.59)	6.27 (6.65)
6	$[Zn(CS_3)_2][Fe(L)_2(H_2O)_2]$ $C_{40}H_{34}ZnFeO_7S_6$	122	51.26 (55.06)	3.33 (3.22)	2.52 (2.50)	6.98 (6.63)	5.67 (6.01)

4. Results and Discussion

4.1 FT-IR spectra

The Absorption band of aromatic (-OH) actually can be seen in IR spectra of ligand 3420 cm^{-1}. This show that just one of the phenolic oxygen from every one of the ligand is deprotonated and engaged with coordination with metal moreover, the band showed up in IR scale 1307 - 1270 cm^{-1} because of IR phenolic C-O stretching in free chalcone ligand has been downward shifted and spectra of the complexes demonstrating the coordination through phenolic oxygen in the bonding of metal are upheld by the presence of new band ν(C-O-M) in range of 865-988 cm-1. The complexes and ligand show IR bands stretching frequency in the range of 2933-3000 cm-1, 2467-2512 cm^{-1}, and 1122-1618 cm^{-1}corresponding for (=CH of Ar), (-CH=CH) and (-C=O) group of the chalcone based ligand and bands at 1287-1318 cm^{-1}, 865-988 cm^{-1} and 765-795 cm^{-1} for (-C=S), (-C-O-M) and (-C-S-M) bands of a tri-thiocarbonate ligand. The presence of coordinates water is also supported by FT-IR spectra of the complexes.

Table 2. FT-IR spectra of the complexes

	Observed frequencies (cm-1)							
Ligand/Complexes	**ν(=CH of Ar)**	**ν(-CH=CH-)**	**ν(-C=O)**	**ν(-C=S)**	**ν(C-O-M)**	**ν(C-S-M)**	**ν(Ar-OH) ν(-OH of H_2O)**	**ν(Ar-OH)**
Ligand (L)	3000	2510	1722	1318				3420
$[Cu(CS_3)_2][Ni(L)_2(H_2O)_2]$	2933	2512	1625	1314	988	778	3020	
$[Cu(CS_3)_2][Co(L)_2(H_2O)_2]$	2980	2499	1618	1298	887	776	3040	
$[Cu(CS_3)_2][Fe(L)_2(H_2O)_2]$	2982	2495	1688	1287	865	787	3005	
$[Zn(CS_3)_2][Ni(L)_2(H_2O)_2]$	2995	2512	1690	1304	912	795	3040	
$[Zn(CS_3)_2][Co(L)_2(H_2O)_2]$	2981	2467	1687	1299	905	760	3010	
$[Zn(CS_3)_2][Fe(L)_2(H_2O)_2]$	2984	2487	1695	1305	897	765	3017	

4.2 NMR spectra

The NMR spectra of the complexes were recorded in DMSO-d_6, ^{1}H & ^{13}C-NMR data are recorded as Table 3. The presence of aromatic proton is confirmed by the multiple in between 7.06 - 8.46 ppm, -CH=CH- band has been confirmed by the signal in a range of 7.10-8.38 ppm. While singlet peak of a hydroxyl group in the ligand (L) at 10.80 but due to complexation (-OH) peak not observed in complexes and ^{13}C-NMR signals appears at the range of 128.00- 164, 114.16 – 148 and 180.02 - 198.48 of (Ar-C), (-C=C- of ethylene carbon) and α,β-unsaturated ketones (-C=O).

Table 3. ^{1}H and ^{13}C-NMR spectral data of complexes

Chemical shift (δ ppm)

Ligand/Complexes	**^{1}H**	**^{13}C-NMR**
Ligand	7.32-8.38 (m, 12H, Ar-H) 11.30 (s, 1H, Ar-OH) 7.60-8.12 (dd, 2H,ethylene-H)	128.20-160.13 ppm (Ar-C) 116.00-146.12 (-C=C- of ethylene carbon) 192.16 (-C=O)
$[Cu(CS_3)_2][Ni(L)_2(H_2O)_2]$	7.22-8.08 (m, 12H, Ar-H) 7.20-8.26 (dd, 2H,ethylene-H)	128.32-158.26 ppm (Ar-C) 114.13-146.15 (-C=C- of ethylene carbon) 188.00 (-C=O)
$[Cu(CS_3)_2][Co(L)_2(H_2O)_2]$	7.12-8.18 (m, 12H, Ar-H) 7.10-8.33 (dd, 2H,ethylene-H)	128.42-160.72 ppm (Ar-C) 115.52-144.62 (-C=C- of ethylene carbon) 180.82(-C=O)
$[Cu(CS_3)_2][Fe(L)_2(H_2O)_2]$	7.30-8.21 (m, 12H, Ar-H) 7.24-8.16 (dd, 2H,ethylene-H)	128.88-165.00 ppm (Ar-C) 114.72-146.66 (-C=C- of ethylene carbon) 192.13 (-C=O)
$[Zn(CS_3)_2][Ni(L)_2(H_2O)_2]$	7.06 -8.46 (m, 12H, Ar-H) 7.16-8.18 (dd, 2H,ethylene-H)	128.02-164.13 ppm (Ar-C) 116.63-142,92 (-C=C- of ethylene carbon) 194.52 (-C=O)
$[Zn(CS_3)_2][Co(L)_2(H_2O)_2]$	7.26-8.36 (m, 12H, Ar-H) 7.10-8.30 (dd, 2H,ethylene-H)	128.19-162.65 ppm (Ar-C) 114.88-146.92 (-C=C- of ethylene carbon) 190.13 (-C=O)
$[Zn(CS_3)_2][Fe(L)_2(H_2O)_2]$	7.30-8.32 (m, 12H, Ar-H) 7.14-8-16 (dd, 2H,ethylene-H)	128.82-165.17 ppm (Ar-C) 118.92-147.54 (-C=C- of ethylene carbon) 191.67 (-C=O)

4.3 Electronic spectra

The UV-Visible spectra show absorbance in the range of 220-480 nm due to n- π* transition of α,β-unsaturated ketones. The compound containing double bond moiety i.e chromophoric group (-C=O) absorbed at higher wavelength due to bathochromic shift. B-band arises due to π -π* transition in aromatic 256 nm.

Table. 4. UV spectra of the complexes

		Absorption (λmax nm)		
Complexes	**Solvent**	**π -π***	**n- π***	**n- π*/CT**
$[Cu(CS_3)_2][Ni(L)_2(H_2O)_2]$	DMSO-d_6	220	258	436
$[Cu(CS_3)_2][Co(L)_2(H_2O)_2]$	DMSO-d_6	240	286	456
$[Cu(CS_3)_2][Fe(L)_2(H_2O)_2]$	DMSO-d_6	240	280	450
$[Zn(CS_3)_2][Ni(L)_2(H_2O)_2]$	DMSO-d_6	234	306	390
$[Zn(CS_3)_2][Co(L)_2(H_2O)_2]$	DMSO-d_6	250	312	440
$[Zn(CS_3)_2][Fe(L)_2(H_2O)_2]$	DMSO-d_6	244	316	480

4.4 Magnetic susceptibility

The magnetic moment values of the complexes are shown in the table. 5. The magnetic moment data obtained by the magnetic susceptibility of complexes suggest square planar geometry of Cu(II), and octahedral geometry of Ni(II), Co(II), and Fe(II).

Table. 5 Magnetic Moment of the metal complexes.

S. No.	**Complexes**	**Magnetic moment (μ) in (B.M)**
1	$[Cu(CS_3)_2][Ni(L)_2(H_2O)_2]$	2.12
2	$[Cu(CS_3)_2][Co(L)_2(H_2O)_2]$	3.01
3	$[Cu(CS_3)_2][Fe(L)_2(H_2O)_2]$	3.61
4	$[Zn(CS_3)_2][Ni(L)_2(H_2O)_2]$	1.02
5	$[Zn(CS_3)_2][Co(L)_2(H_2O)_2]$	2.08
6	$[Zn(CS_3)_2][Fe(L)_2(H_2O)_2]$	3.19

4.5. Solid state electrical conductivity

The temperature-dependent solid-state electrical conductivity of the complexes exhibit the semiconducting nature of the complexes. There is an increase in conductivity with an increase in temperature. It can be suggested that this behavior is due to the presence of exocyclic sulfur of CS_3^{2-} which form short M---S and S---S interaction.

Table 6. Solid state electrical conductivity σ_{rt} (Scm^{-1})

S. No.	Complex	Temperature (°C)				
		30	40	50	60	70
1	Cu-Ni	2.9×10^{-5}	3.9×10^{-5}	4.8×10^{-5}	5.6×10^{-5}	9.2×10^{-5}
2	Cu-Co	3.2×10^{-6}	3.5×10^{-6}	4.1×10^{-6}	7.0×10^{-6}	7.8×10^{-6}
3	Cu-Fe	2.1×10^{-5}	2.8×10^{-5}	3.8×10^{-5}	4.3×10^{-5}	6.1×10^{-5}
4	Zn-Ni	4.2×10^{5}	4.7×10^{5}	5.9×10^{5}	7.8×10^{5}	8.8×10^{5}
5	Zn-Co	4.0×10^{-9}	3.8×10^{-9}	5.3×10^{-9}	6.5×10^{-9}	7.2×10^{-9}
6	Zn-Fe	2.6×10^{-7}	3.3×10^{-7}	4.7×10^{-7}	5.9×10^{-7}	9.3×10^{-7}

4.6 Powder XRD Spectra

The Powder X-ray diffraction patterns of the complexes are shown in Figures 2-3. The small variation in 2Θ, d-spacing, lattice strain, crystallite size, and the peak intensity in the patterns have been observed. The powder XRD diffraction of the sample is used to determine the crystallinity of the complexes by comparison of background patterns to that of sharp peaks. Powder XRD pattern (Figures- 2 and 3) of the complexes show their crystalline nature of the complexes.

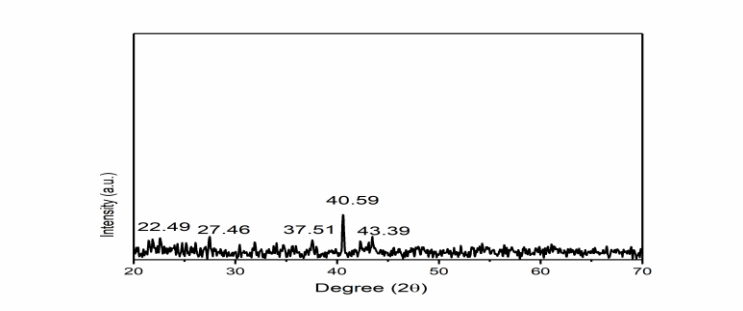


Fig. 2 $[Cu(CS_3)_2][Ni(L)_2(H_2O)_2]$

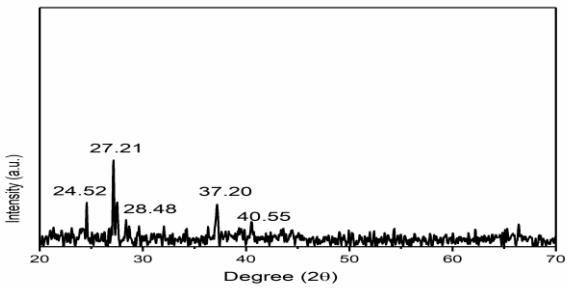
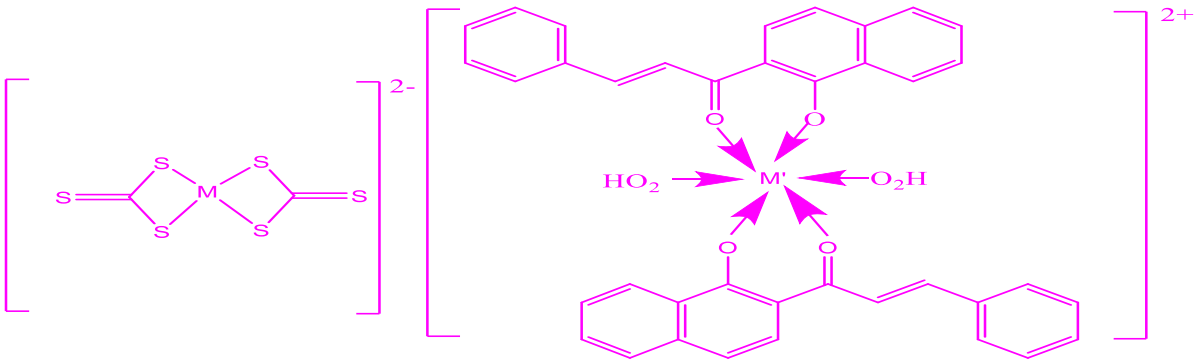


Fig. 3 $[Zn(CS_3)_2][Ni(L)_2(H_2O)_2]$

5. Conclusion:

In accordance with the magnetic susceptibility measurements and electronic absorption data, the anionic metallo ligand $[M(CS_3)^{2-}]$ [M= Cu(II) or Zn(II)] the central metal atom is aspected to be square planar geometry. In the case of the cationic part of the complex salt, it is assumed to be octahedral geometry around the central metal atom [Fe(II)/ Ni(II) or Co(II)]. The presence of coordinated water is supported by a peak in the IR region. The temperature-dependent solid-state conductivity results show that these compounds are semiconducting. There is an increase in conductivity with a stepwise increase in temperature has been observed. Probity there is M---S, and S---S interaction responsible for conductivity. Proposed structure of the complexes as follows:



where [M= Cu(II), Zn(II) and M′= Fe(II), Ni(II), Co(II]

Figure. 4 Proposed structure of the complexes

6. Acknowledgement:

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