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Design of some novel dithio π-conjugated ligand-based metal complexes and their semiconductor behavior

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***Abstract*---**Transition metal complexes with sulfur-based ligands are the area of interest for scientists working for semiconducting molecular materials. These complexes have been reported for their interesting electronic architecture and can be used in the manufacture of various kinds of electronic devices including diodes, transistors and integrated circuits. The nitrophenol thiourea benzaldehyde-based metal complexes with various transition metals have been reported for their electrical behavior. The present paper involves synthesis, spectroscopic characterization and variable temperature solid-state conductivity measurement. The complexes show semiconducting nature.

***Keywords*---**Semiconductor, NPBT, Solid-state conductivity, solution conductivity.

Introduction

Dithio ligands with the π-conjugated system[1]–[4] are important for the designing of electronic molecular materials. In this context, these complexes of mcda^{-2} ligand are expected to have promising features for its application as an inorganic metal complex for semiconductor and electronic industrial uses[5]–[9]. The phenol-based thiourea benzaldehyde ligand was also attracted for this type of study[10]. Therefore, in the present work, the incorporation of both these ligands

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with various transition metals is taken under consideration. The mixed ligand complexes of transition metals have been an interesting area of research for scientists working with coordination complexes and their versatile applications[11]–[15]. Several mononuclear and binuclear homo se well as heterobimetallic complexes, complex salts and coordination poly materials have been reported[16]–[18].

Experimental

Materials and Methods

The chemicals we used in the entire work were obtained from Merk and of AR grade. The solvents were purified before use.

Preparation of K_2mcda ligand

The potassium-(1-methoxy-carbonyl)-1-cyano ethylene-2,2 dithiolate salt (K$_2$mcda) was prepared using the reported method. The solution of 0.1 mole of methyl cyanoacetate and 0.1 mole CS_2 was added to the suspension of 0.2 mol potassium hydroxide in 100 ml dioxane. During the addition, the solution was stirred and the temperature was maintained at 15-20 °C. After complete addition, the reaction mixture was further stirred for about half an hour and approximately 250 ml of ether was added for dilution. The yellow-colored precipitate was filtered off and finally washed with a 9 1: 1 solution of dioxane and ether and dried in a vacuum.

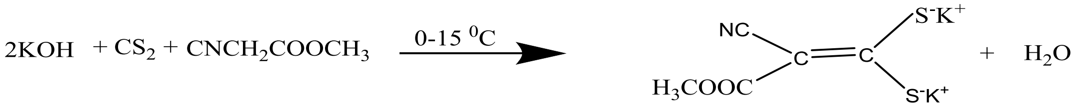
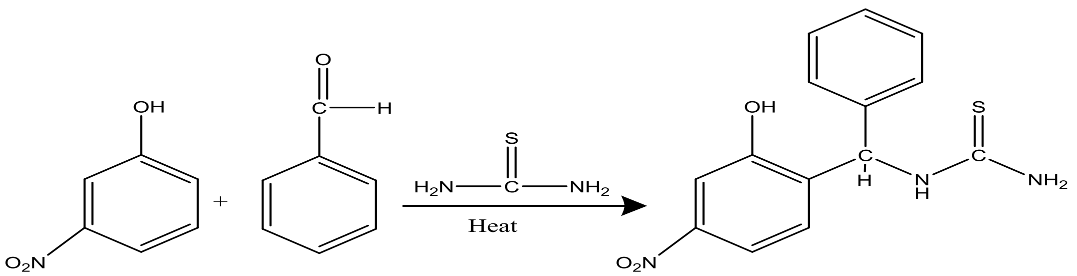


Fig. 1. Preparation of K$_2$mcda ligand

Preparation of 3-nito-phenol-benzaldehyde-thiourea (NPBT) ligand

In a round bottom flask, the mixture of 0.2 mole of 3-nitrophenol and 0.2-mole benzaldehyde was taken and a solution of 0.2 mole of thiourea in ethanol was added drop by drop with constant stirring. The contents of the mixture were further stirred for 5 hours. The colloidal product obtained was kept overnight in the refrigerator. The dark brown solid was washed with ether and recrystallized from ethanol [Fig. 2].



3-nitro-phenol-benzaldehyde thiourea based (NPBT) ligand

Fig. 2 Preparation of 3-nitro-phenol-benzaldehyde-thiourea based (NPBT) ligand.

Preparation of complexes

Preparation of [Co(NPBT)$_2$(mcda)] complex: Cobalt (II) chloride in water, K$_2$mcda in water and NPBT ligand in ethanol in the ratio of 1:1:1(v/v) were taken and mixed with constant stirring up to 20 min. then the product formed was filtered off and dried over the vacuum.

$K_2mcda + CoCl_2 + 2NPBT \rightarrow 2KCl + [Co(NPBT)_2(mcda)]$

Preparation of [Cu(NPBT)(mcda)], [Ni(NPBT)(mcda)] and [Zn(NPBT)(mcda)] complexes: The ethanolic solution of NPBT ligand and aqueous solution of K$_2$mcda was added to an aqueous ethanolic solution of metal salts (copper sulfate/ nickel sulfate / zinc acetate) in the ratio 1:1:2 by volume with constant stirring up to 2 hours to complete the reaction. The product formed was filtered off and dried over the vacuum.

$MX_2 + K_2mcda + NPBT \rightarrow 2KX + [M(mcda)(NTBT)]$

Where M= Cu(II), Ni(II) and Zn(II)

Preparation of [Cr(NPBT)$_2$(mcda)].Cl Complex : Ligands K$_2$mcda and NPBT was taken in ethanol and CrCl$_3$.6H$_2$O was also taken in ethanol in the ratio 1:2:1 by volume and the contents were stirred up to 6 hours. The product thus formed was filtered off, washed several times with water and dried over the vacuum.

$K_2mcda + CrCl_3.6H_2O + NPBT \rightarrow 2KCl + 6H_2O + [Cr(mcda)(NPBT)_2].Cl$

Analysis and Physical Measurements

The ligands and complexes were analyzed for elemental analysis. C, H and N were tested at Jiwaji University Gwalior using Carlo Erba 1108 element analyzer. The sulfur and transition metals were analyzed in our laboratory by gravimetric methods. The molar conductivity of the complexes was determined in DMSO solution using a Systronics conductivity meter with the platinum electrode. FT-IR spectra were determined using Perkin Elmer model Spectrum two Series no.-105627 FT-IR at Jiwaji University, Gwalior, ^{1}H and ^{13}C study have been done on 400 MHz spectrometer at IIT Delhi, U.V. visible spectra have been performed on UV-1280 multipurpose UV-Vis. A spectrometer in DMSO at Jiwaji University., Gwalior. The magnetic behavior study was performed on Cahn-Faraday electro balance and [CoHg(SCN)$_4$] was used as standard. Solid-state conductivity were measured at Schlumberger impedance gain phase analyzer.

Table 1
Analytical results and general behavior of the complexes

S.No.	Complexes	Colour (% yield)	M.P. or D.P.(^{0}C)/ solubility	C%	H%	N%	S%	M%
1	[Co(mcda)(NPBT)$_2$]	Brown(75)	271-275/DMF	Cal. 47.25 Obs. (47.15)	3.48 (3.45)	11.69 (11.53)	15.29 (16.09)	7.03 (7.00)
2	[Cu(mcda)(NPBT)]	Dark Brown(80)	278-280/DMF	42.26	2.96	10.37	17.79	11.77

				(42.20)	(2.90)	(10.35)	(17.72)	(11.79)
3	[Ni(mcda)(NPBT)]	Brown(70)	275-280/DMF	42.64 (42.42)	3.01 (3.00)	10.47 (10.42)	17.97 (17.90)	10.97 (10.85)
4	[Cr(mcda)(NPBT)$_2$]Cl	Brown(77)	269-270/DMF	45.70 (45.65)	3.37 (3.27)	11.30 (11.29)	14.79 (14.70)	6.00 (6.00)
5	[Zn(mcda)(NPBT)]	Brown(67)	281-285/DMF	42.11 (42.10)	2.95 (2.90)	10.34 (10.30)	17.73 (17.55)	12.07 (12.00)

Ligand (L or NPBT). Yield 75%, m.p. 240-255 ^{0}C, Dark brown solid**,** FT-IR (KBr, ν cm^{-1}): 3400 (-CH, Ar), 1600 (-C=C-, Ar), 3350, (-N-H, str), 1330 (Ar-NO$_2$), 1039 (C=S)

^{1}H-NMR (400 MHz, DMSO, □ ppm) 7.1-8.0 ppm (m 8H, Ar-H of phenyl and phenolic ring), 6.0 ppm (s, 1H, phenolic-OH), 4.5 ppm (s, 2H,NH$_2$ broad lines), 3.38 ppm (d, 1H, CH attached to phenyl and phenolic ring),

^{13}C-NMR (400 MHz, DMSO, □ ppm) 6.72 ppm (CH), 128.0-137.6 (Ar-C), 158.1-162.2 (C=S), 208.5 (C-S)

Ligand (mcda^{2-}).
FT-IR (KBr, ν cm^{-1}): 1619.05 (-C=C-), 2195.02 (–CN), 1840 (CO, conjugated), -1193.24 (-C-O) , 790 –C=S), conjugated)

^{1}H-NMR (400 MHz, DMSO, □ ppm) 3.5 (s, of **-**OCH$_3$),

^{13}C-NMR (400 MHz, DMSO, □ ppm) 116 (-C=C-), 180 (-CO) 45 (-CH$_3$)

[Co(mcda)(NPBT)$_2$].
FT-IR (KBr, ν cm^{-1}): 2195 (–CN), 750 (-C-S), 1620 (-C=C-), 1845 (-C=O, ester), 1193 (-C-O, ester), 1531 (-C=C-, Ar), 3350 (-N-H str), 1330 (Ar-NO$_2$), 3400 (Ar-OH), 700-800 (Ar-CH).
UV-Visible (DMSO, Absorption (λmax) nm), 450-510 nm

[Cu(mcda)(NPBT)].
FT-IR (KBr, ν cm^{-1}): 2204 (–CN), 649 (-C-S), 1620 (-C=C-), 1845 (-C=O, ester), 1193 (-C-O, ester), 3400 (-CH, Ar), 1527 (-C=C-, Ar), 3393 (-N-H str), 1331.56 (Ar-NO$_2$), 3400 (Ar-OH), 700-800 (Ar-CH).
UV-Visible (DMSO, Absorption (λmax) nm), 450-460 nm

[Ni(mcda)(NPBT)].
FT-IR (KBr, ν cm^{-1}): 2201 (–CN), 649 (-C-S), 1621 (-C=C-), 1842 (-C=O, ester), 1193 (-C-O, ester), 3400 (-CH, Ar), 1524 (-C=C-, Ar), 3392 (-N-H str), 1324 (Ar-NO$_2$), 3400 (Ar-OH), 700-800 (Ar-CH, o,m,p).

UV-Visible (DMSO, Absorption (λmax) nm), 430-550 nm

[Cr(mcda)(NPBT)$_2$]Cl
FT-IR (KBr, ν cm^{-1}): 2204 (–CN), 614 (-C-S), 1650 (-C=C-), 1789 (-C=O, ester), 1197 (-C-O, ester), 3400 (-CH, Ar), 1531 (-C=C-, Ar), 3359 (-N-H str), 1332 (Ar-NO$_2$), 3400 (Ar-OH), 700-800 (Ar-CH).
UV-Visible (DMSO, Absorption (λmax) nm), 424-510 nm

[Zn(mcda)(NPBT)].
FT-IR (KBr, ν cm^{-1}): 2214 (–CN), 748 (-C-S), 1620 (-C=C-), 1842 (-C=O, ester), 1193 (-C-O, ester), 3400 (-CH, Ar), 1523 (-C=C-, Ar), 3436 (-N-H str), 1330 (Ar-NO$_2$), 3400 (Ar-OH), 700-800 (Ar-CH).
UV-Visible (DMSO, Absorption (λmax) nm), 410- 505 nm

Result and Discussion

The element detection results are indicative of the composition of complexes [Co(mcda)(NPBT)$_2$], [Cu(mcda)(NPBT)], [Ni(mcda)(NPBT)], [Cr(mcda)(NPBT)$_2$]Cl and [Zn(mcda)(NPBT)]. The complexes are insoluble in water and soluble in DMF. The recrystallization of complexes cannot be done. The purity of compounds were confirmed by T.L.C., powder XRD spectra were recorded using fifth-generation Rigaku model no. mini flex 600 at central instrument facility, Jiwahi University, Gwalior.

FT-IR-

The Infra-Red bands at approximately 1600cm^{-1} (-C=C -Ar), 3350 cm^{-1} (-NH), 1330 cm^{-1} (Ar-NO$_2$) and at 1039 cm^{-1} (-C=S), for phenolic ligand moiety of the complex has been confirmed. The absorption band at around 1620 cm-^{1} (-C=C-), 2200 cm^{-1} (-CN), 1840 cm^{-1} (-C=O conjugated) 1200 cm^{-1} (C-O), and at 790 cm^{-1} for M-S and M-N suggest that metal-ligand complexion occurs through S of mcda^{-2} and N and S of thiourea moiety of phenolic ligand. The absence of free -NH$_2$ group in complexes also supports complexation via a nitrogen of the thiourea group of the ligand.

NMR spectra

^{1}H and ^{13}C NMR spectra of ligand NPBT and mcda^{-2} has been shown in [figure. 3 and Table 3]. For NPBT ligand the peaks at 7.1-8.0 ppm (m, 8H), 6.0 ppm (d, 1H), 4.5 ppm (broad peak) and 3.38 ppm (d, 1H) for phenolic -OH, -NH and NH$_2$ of thiourea moiety and -CH attached to phenyl and phenolic ring. ^{13}C-NMR peaks for this ligand have been observed at 56.72 ppm, 128-137.6 ppm,158.1-162.2 ppm and 208.5 ppm for -CH, AR-C, C=S and C-S respectively. Similarly, in the case of mcda^{-2} ligand the ^{1}H-NMR peaks at 3.5 ppm (s, 3H) have been observed for (-OCH$_3$) while peaks for ^{13}C-NMR signals have been observed at 45 ppm,180 ppm and 116.0 ppm for -CH$_3$, -COCH$_3$ and C=C respectively.

Electronic adsorption spectra

The electronic spectra of the complex were recorded in DMSO. The absorption band in the region of 255-268 nm and 290-330 nm is due (π-π*) transition and due to the B band of the benzenoid ring structure and (C=C) group. The absorption peaks in the range of (369-438) nm arise due to (n-π*) transition. The octahedral geometry of Co(II) and Cr(III), square planer geometry around Cu(II), Ni(II) and Zn(II) have been reported [Fig.-3].

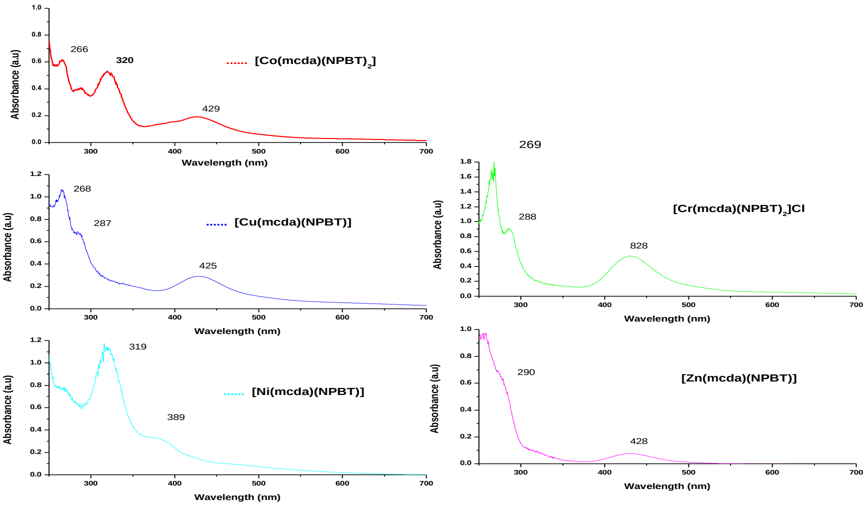


Fig. 3. UV spectra of the complexes

Magnetic moment and solution Conductivity

The magnetic behavior of the complexes were determined by the measurement of magnetic susceptibility of these complexes. The magnetic data for these complexes are shown in [Table 2]. The values suggest that Co(II), Cu(II), Cr(II) and Ni(II) are paramagnetic while Zn(II) shows diamagnetic behavior. Molar conductivity results show that [Cr(mcda)(NPBT)$_2$]Cl shows 1:1 electrolytic behavior while other complexes of this series are coordination complex of non-electrolytic nature.

Powder XRD spectra

The powder XRD spectra analysis insists we conclude that the Co(II) complex is crystalline and shows somewhat specific pattern different from other complexes of the series. Cu(II) and Ni(II) complexes are also crystalline and somewhat similar in structural aspects, but Cr(III) complex shows an XRD spectral pattern quite different than the above previous members of this series. This is probably due to the 1:1 electrolytic nature of complex salt as evident from the solution conductivity result. The Zn(II) complex shows an amorphous powder XRD spectrum.

Solid State Conductance Measurement

The complexes were studied for their solid-state conductivities at various temperatures (30°-80℃). The current against the voltage was noted for each stepwise increase of voltage. Repeated measurements were taken starting from room temperature 30° to 80℃ by increasing 10℃ in a stepwise manner. The resistance observed were converted to the specific conductance and the plot of the log of specific conductance versus inverse of temperature were plotted. There is an increase in conductivity with an increase in temperature reflects that these complexes are semiconducting.

Magnetic Susceptibility

The magnetic moment values are somewhat calculated for the number of electrons present in individual metals of the complexes (Table-2). This strongly recommends that the composition of complexes is correct.

Table 2
Magnetic Moment of the metal complexes

S. No.	Complexes	Magnetic moment (μ) in (B.M)	Molar Magnetic Susceptibility (x_m)
1	$[Co(mcda)(NPBT)_2]$	4.60	0.00889
2	[Cu(mcda)(NPBT)]	1.86	0.00145
3	[Ni(mcda)(NPBT)]	3.70	0.00574
4	$[Cr(mcda)(NPBT)_2]Cl$	3.90	0.00638
5	[Zn(mcda)(NPBT)]	0.00	-

Electrical conductance

The electrical conductivity of the solid-state of these complexes is recorded at variable temperatures starting from 30 ^{0}C to 70 ^{0}C, with each phase increasing by 10 ^{0}C. The plot for the specific conductivity is plotted against 1/T in [Table. 3]. The increase in conductivity with an increase in temperature suggests the semiconductivity behavior of these complexes. The bandgap was observed in the range of 0.85 to 2.20 eV.

Table 3
The complexes solid-state conductivity

S. No.	Complexes	Solid-state electrical conductivity σrt (Scm^{-1})
1	$[Co(mcda)(NPBT)_2]$	3.162×10^{-4}
2	[Cu(mcda)(NPBT)]	1.949×10^{-1}
3	[Ni(mcda)(NPBT)]	7.943×10^{-2}
4	$[Cr(mcda)(NPBT)_2]Cl$	9.77×10^{-3}
5	[Zn(mcda)(NPBT)]	1.527×10^{-1}

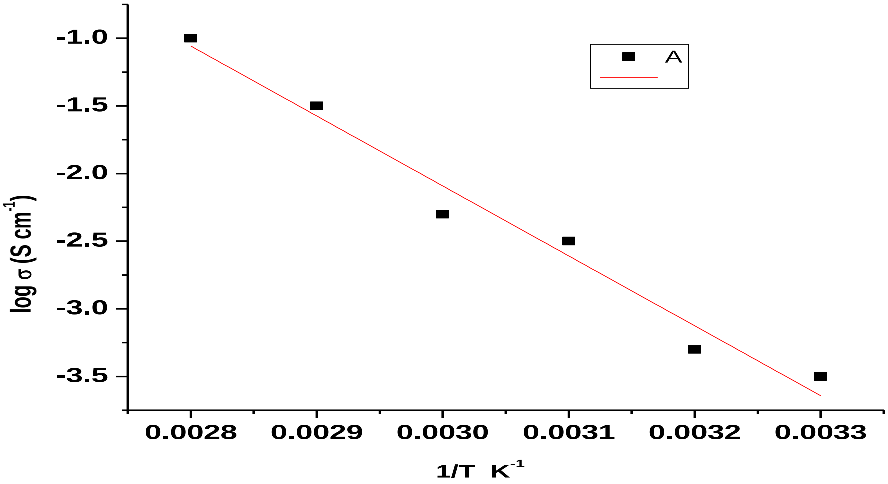


Fig.4 Solid-state conductivity of the complex [Co(mcda)(NPBT)$_2$]

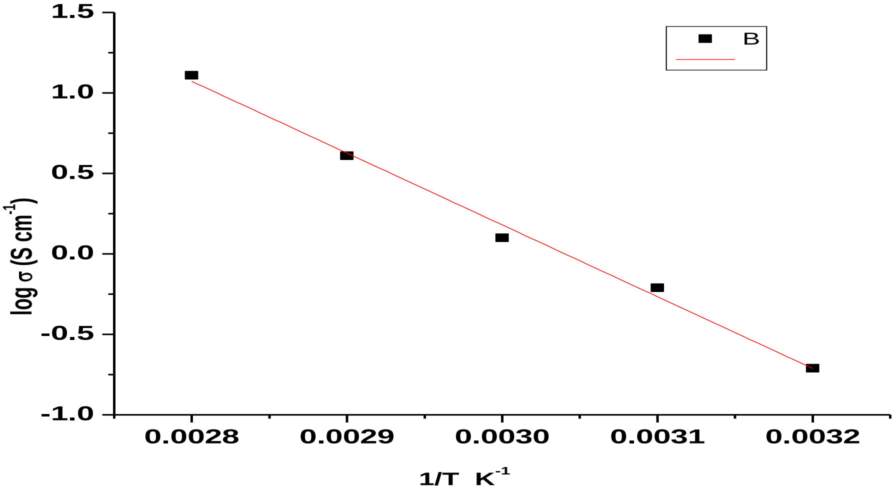


Fig.5 Solid-state conductivity of the complex [Cu(mcda)(NPBT)]

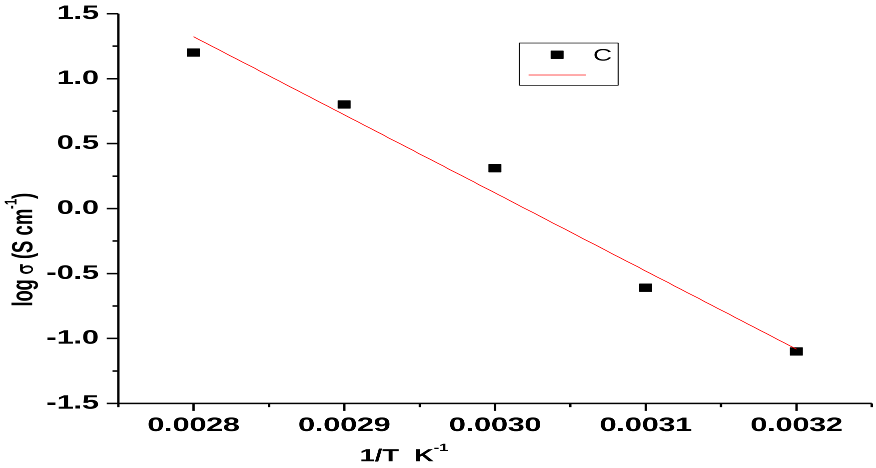


Fig.6 Solid-state conductivity of the complex [Ni(mcda)(NPBT)]

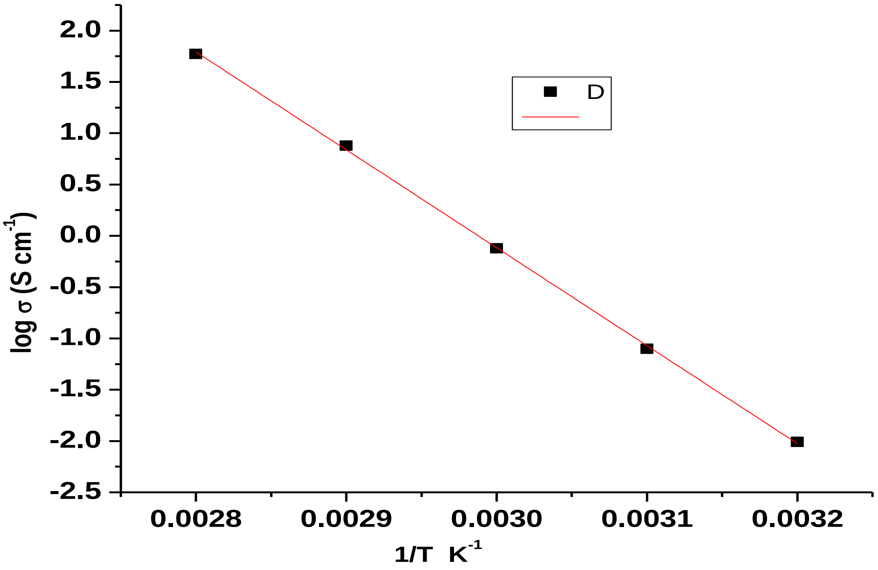


Fig.7 Solid-state conductivity of the complex [Cr(mcda)(NPBT)$_2$]Cl

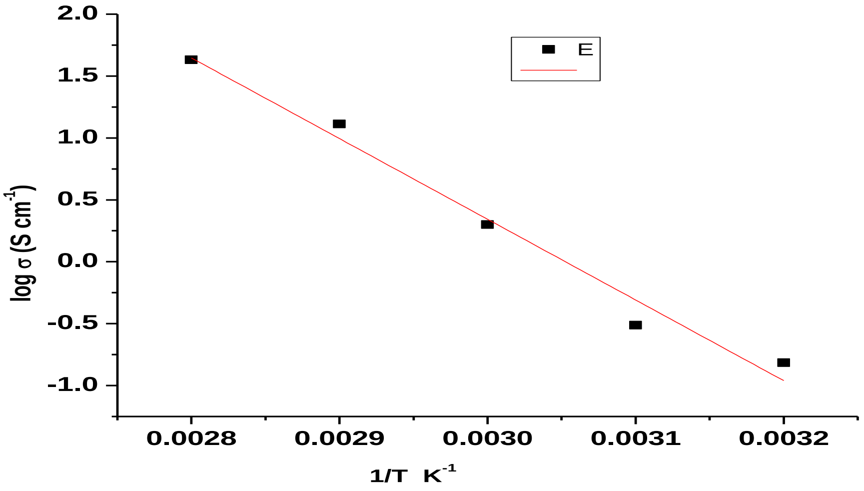


Fig. 8 Solid-state conductivity of the complex [Zn(mcda)(NPBT)]

Conclusion

The transition metal complexes of mixed ligand NPBT and mcda^{-2} are semiconducting. The spectroscopic results obtained from IR results suggest that metal-ligand bonding occurs through M-S and M-N bonds in the case of NPBT ligand, while through M-S bond for mcda^{-2} ligand. Similarly, the NMR results of the ligand support the structure of both these ligands as mentioned in our proposed structure of the complexes in (fig. 9-11). The electronic absorption spectra, magnetic moment data and solution conductivity values suggest that coordination of Co(II) and Cr(III) are octahedral while Cu(II), Ni(II) and Zn(II) are square planar in these complexes. The oxidation state of chromium is +3 and the complex exists as complex salt. The powder X-ray spectra of these complexes show their crystalline nature except for Zn(II). The conductivity measurements in a temperature programmable manner suggest that the complexes are semiconductor molecular materials. This may be due to sulfur-sulfur interaction or may be due to metal-metal and metal-sulfur interaction between the layered lattice structure of the complexes.

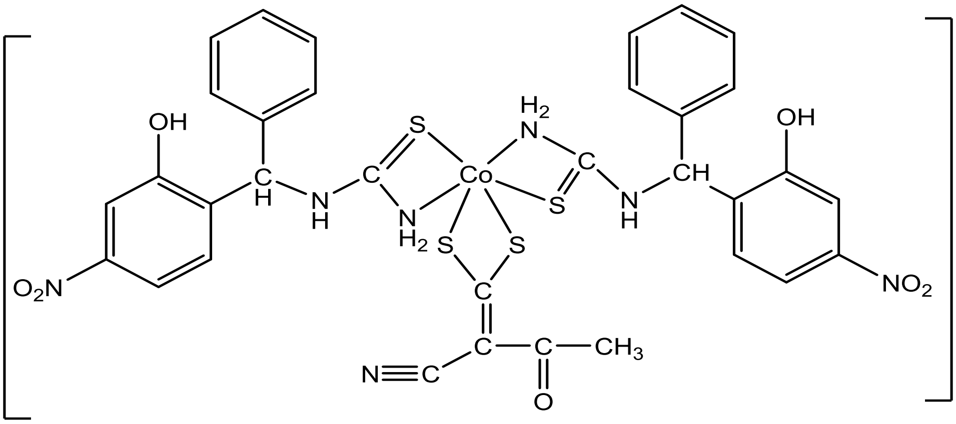


Fig. 9 Proposed structure of the complex [Co(NPBT)$_2$(mcda)]

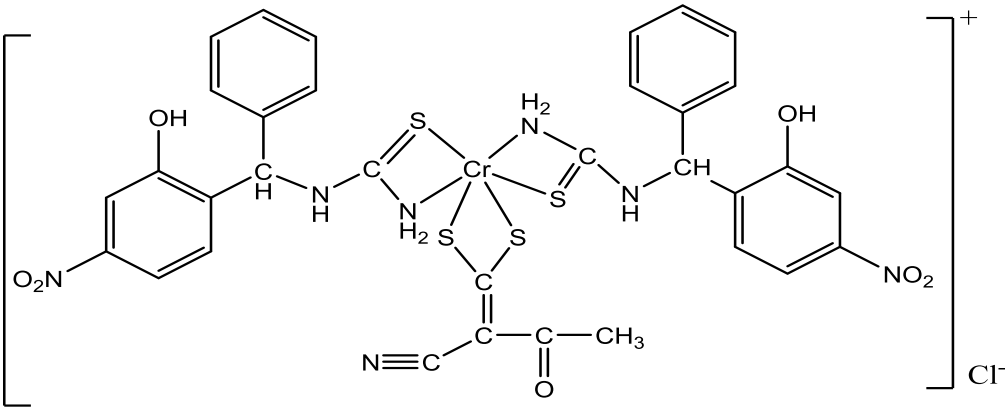


Fig. 10 Proposed structure of the complex [Cr(NPBT)$_2$(mcda)]Cl$^-$

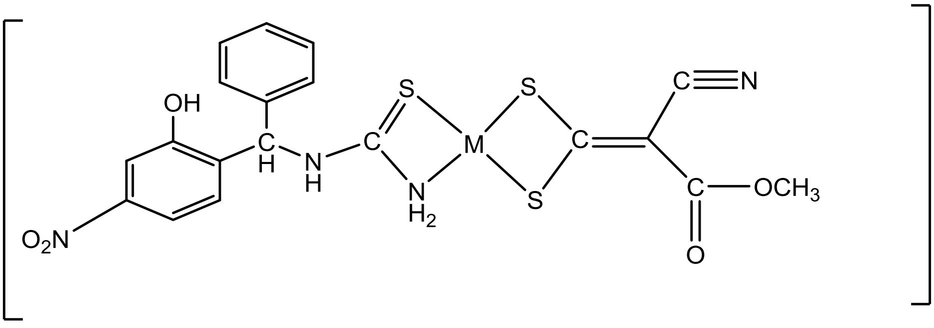


Fig. 11 Proposed structure of the complexes [M(NPBT)(mcda)]
Where M= Cu(II), Ni(II) and Zn(II)

Acknowledgments

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