

Design and Spectroscopic Characterization of some Novel Tetrazolium Formazan Based Transition Metal Complexes.

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Abstract

The formazan tetrazolium systems are reported for their special structural aspects and their applications in medicinal field. The electronic architecture of formazone can also be used for the synthesis of electronic, optical and photovoltaic materials of multiple interest. In the present work our focus is mainly on the synthesis and spectroscopic characterization of some new mixed ligand transition metal complexes of formazon tetrazolium system.

Introduction

Several reviews [1,2] are reported on the versatile structural aspects of the formazans as well as of tetrazolium salts. In general, the tetrazolium salts are colourless but when they are reduced to their corresponding formazan seems coloured because they show $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transition in the visible region [3,4]. Formazan and tetrazolium can be used as redox ligand. The formazans can be obtained by the reduction of tetrazolium salt and by the oxidation of formazans tetrazolium salt can be obtained. Gilroy reported the dehydrogenase inhibition activity investigation by formazans. The opto electronic property of these systems are also investigated by several research groups. formazans have four geometrical isomeric forms i.e. cis-syn, cis- anti, trans-syn, and trans-anti [5,6] The delocalization of double bonds in the tetrazolium ring structure can have different patterns [7-9]. The thiocyanate ligand is a mono dentate thio ligand. We have used thiocyanate as the second ligand with formazan in the formation of metal complex [10,11].

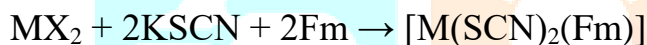
Experimental

Materials and methods

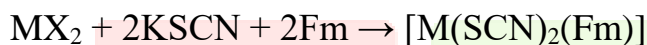
The chemicals triphenyl tetrazolium salt, potassium thiocyanate and transition metal salts were purchased from Merk chemicals. All reagents are of analytical grade.

Preparation of complexes

Under the reaction medium the tetrazolium salt gets reduced to formazan. The aqueous solution of metal salts (manganese acetate / cobalt chloride / nickel sulphate / zinc chloride / copper sulphate) and ethanolic solution of triphenyl tetrazolium chloride and aqueous solution of potassium thiocyanate was mixed together in appropriate molar ratio and stirred for 2hr at room temperature. The products obtained were filtered off and washed with cold water and dried under vacuum.



Where, M = Co(II) / Ni(II) / Mn(II) , Fm = Formazan



Where, M = Cu(II) / Zn(II) , Fm = Formazan

Scheme for the preparation of Complexes.

Analysis and physical studies

All the complexes were analyzed for elements C, H and N on carlo Erba 1108 element analyzer. FT-IR spectra were determined on perkin Elmer model no. 2 spectrum series no. 105627. FT-IR. Both studies have been done at jiwaji university, Gwalior. ¹H and ¹³C-NMR data were collected on 400 MHz spectrometer at IIT, Delhi, UV- Spectra of the complexes were obtained on UV-1280 multipurpose UV-visible spectrometer in DMF at jiwaji university, Gwalior. The magnetic moment data were collected on Cahn Faraday electro balance.

Result and discussion

The general behaviour of the complexes complexes and results of analytical determinations are summarized in table.1-3

Table.1 Analytical Results of the complexes

| S.N. | Complex | Colour | M.P.(⁰ C)/ Solubility | C% | H% | N% | S% | M% | Molar mass |
|------|---|------------|--------------------------------------|-------|------|-------|------|------|---------------|
| 1. | [Mn(Fm) ₂ (SCN) ₂] | yellow | 100/DMF | 57.01 | 3.80 | 16.62 | 7.60 | 6.52 | 841.90 |
| 2. | [Co(Fm) ₂ (SCN) ₂] | Sky blue | 300/DMF | 56.74 | 3.78 | 16.54 | 7.56 | 6.96 | 845.93 |
| 3. | [Fe(Fm) ₂ (SCN) ₂] | Pink | 240/DMF | 56.75 | 3.78 | 16.55 | 7.57 | 6.93 | 845.69 |
| 4. | [Cu(Fm)(SCN) ₂] | Yellow | 120/DMF | 56.57 | 3.53 | 16.49 | 7.54 | 7.48 | 848.50 |
| 5. | [Zn(Fm)(SCN) ₂] | colourless | 310/DMF | 56.44 | 3.52 | 16.46 | 7.52 | 7.68 | 850.38 |

Table.2 FT-IR Data of complexes (in cm⁻¹)

| S.N. | Ligand/Complex | C=N(cm ⁻¹) | N-H | N=N | C-S | Ar(C=C) | M-S | M-N | Ar(C-H) |
|------|---|------------------------|------|------|-----|---------|-----|-----|---------|
| 1. | Fm | 1510 | 3020 | 1370 | - | 1600 | - | - | 3100 |
| 2. | SCN | - | - | - | 770 | - | - | - | 3090 |
| 3. | [Mn(Fm) ₂ (SCN) ₂] | 1522 | 3091 | 1365 | 695 | 1575 | 772 | 553 | 3095 |
| 4. | [Co(Fm) ₂ (SCN) ₂] | 1527 | 3098 | 1342 | 740 | 1581 | 760 | 563 | 3090 |
| 5. | [Fe(Fm) ₂ (SCN) ₂] | 1523 | 3092 | 1368 | 722 | 1505 | 781 | 565 | 3090 |
| 6. | [Cu(Fm)(SCN) ₂] | 1529 | 3093 | 1385 | 720 | 1540 | 784 | 550 | 3092 |
| 7. | [Zn(Fm)(SCN) ₂] | 1520 | 3095 | 1402 | 735 | 1531 | 778 | 554 | 3093 |

Table.3 NMR Data of the complexes

| S.N. | Ligand/Complex | ¹ H(ppm) | ¹³ C(ppm) |
|------|---|---------------------|---|
| 1. | Fm | 6.8m, Ar-H | 142ppm (Ar-C),65ppm (C-attached to Ar ring,122 ppm (-CN)) |
| 2. | [Mn(Fm) ₂ (SCN) ₂] | 6.6m, Ar-H | 148ppm (Ar-C),66ppm (C-attached to Ar ring,120 ppm (-CN)) |
| 3. | [Co(Fm) ₂ (SCN) ₂] | 6.5m, Ar-H | 140ppm (Ar-C),60ppm (C-attached to Ar ring,123 ppm (-CN)) |
| 4. | [Fe(Fm) ₂ (SCN) ₂] | 6.7m, Ar-H | 145ppm (Ar-C),68ppm (C-attached to Ar ring,125 ppm (-CN)) |
| 5. | [Cu(Fm)(SCN) ₂] | 6.8m, Ar-H | 144ppm (Ar-C),65ppm (C-attached to Ar ring,126 ppm (-CN)) |
| 6. | [Zn(Fm)(SCN) ₂] | 6.9m, Ar-H | 140ppm (Ar-C),64ppm (C-attached to Ar ring,122 ppm (-CN)) |

FT-IR Spectra

Some notable infrared absorption peaks for -C=N, N-H, and N=N functional moieties in between 1520 to 1527 cm⁻¹, ~3091 to 3098 cm⁻¹ and 1342 to 1402 cm⁻¹ suggest that Complex, [Mn(Fm)₂(SCN)₂], [Co(Fm)₂(SCN)₂] and [Fe(Fm)₂(SCN)₂] shows octahedral chelate structure while [Cu(Fm)(SCN)₂] and [Zn(Fm)(SCN)₂] show square planer chelate structure. The details of absorption peaks are mentioned in table-2. The spectra were recorded in KBr pellets.

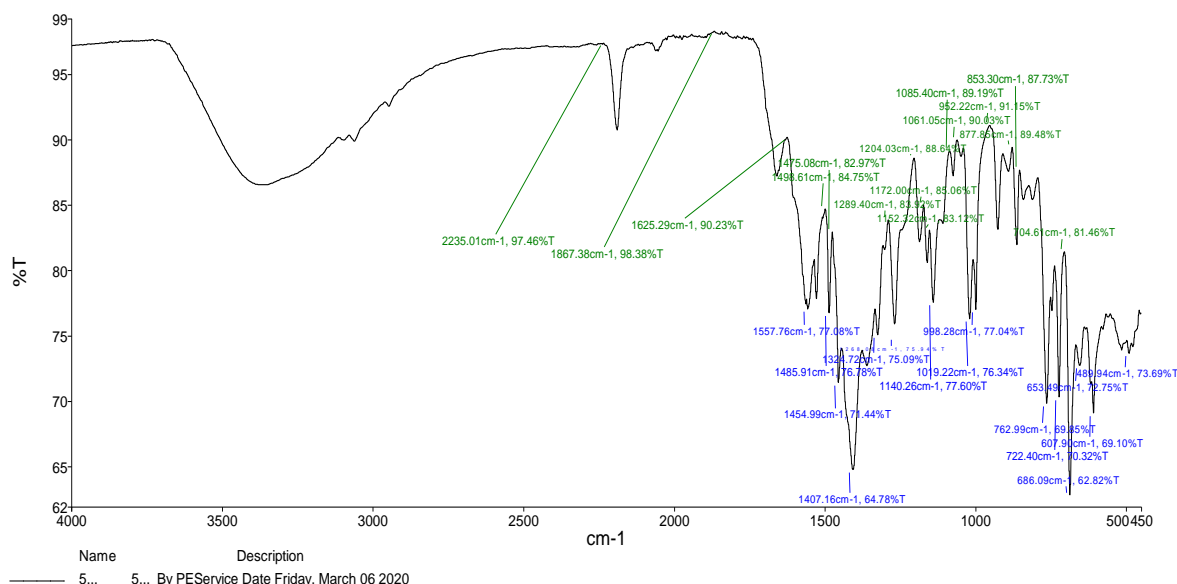


Fig.1 IR-Spectra of the complex $[\text{Fe}(\text{Fm})_2(\text{SCN})_2]$

NMR spectra

¹H NMR spectra of the complexes recorded in DMSO-d₆. The peaks for aromatic protons at 6.53 and 7.82 ppm due to aromatic protons while at 3.79 ppm due to N-H proton. All the spectra were recorded in DMSO-d₆.

Electronic spectra

The complexes are analyzed for UV-visible spectral analysis in chloroform. Four different types of absorptions are noticed. First (200-235nm), second (240-290nm), third (300-380nm) in UV range and fourth peak within 400-600nm in visible region. The first three are due to $\pi \rightarrow \pi^*$ transition in phenyl group while the fourth one is due to charge transfer transition.

Powder XRD spectra

The powder XRD data of the complexes shows that the complex $[\text{Fe}(\text{Fm})_2(\text{SCN})_2]$ and $[\text{Mn}(\text{Fm})_2(\text{SCN})_2]$ are somewhat amorphous and showing no any sharp peaks.

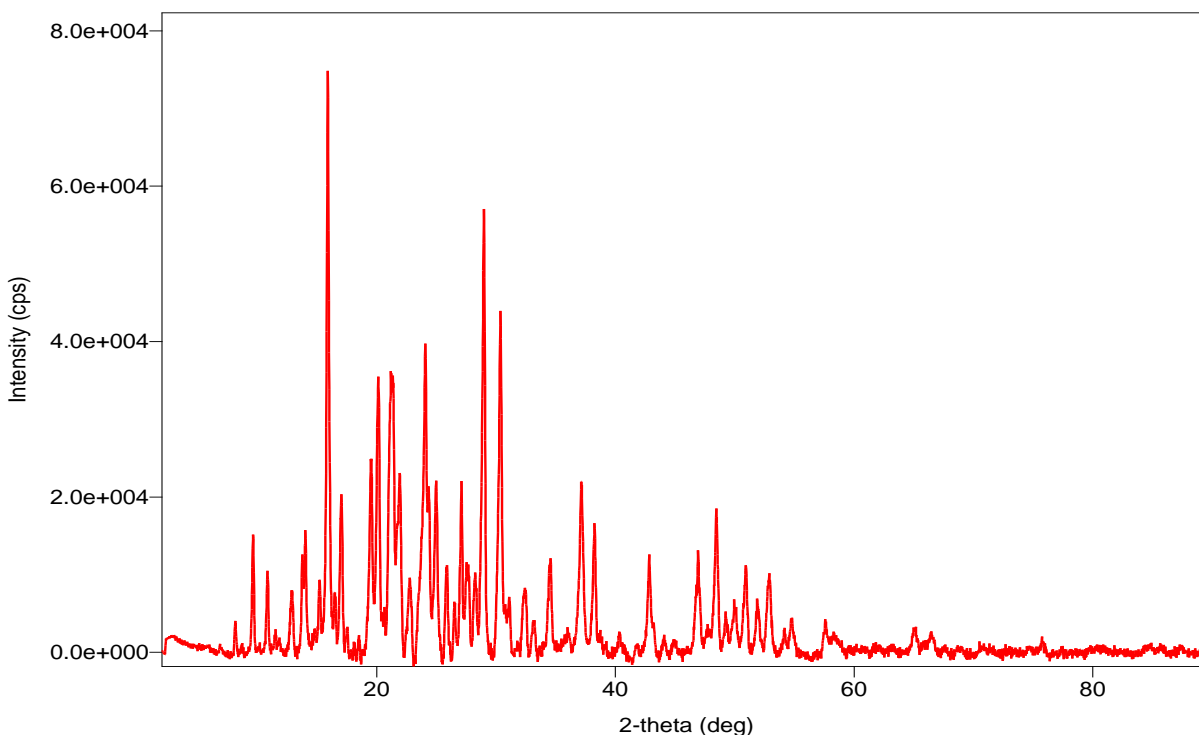


Fig.2 Powder XRD Spectra of the complex [Fe(Fm)₂(SCN)₂]

Magnetic moment

The magnetic behaviour of complexes reveal that complexes of Mn(II), Fe(II) and Co(II) are in accordance with their octahedral geometry in their complexes. The magnetic moment value of the complexes also in support of the paramagnetic broadening of ¹H- NMR peaks. The magnetic moments of the complexes are reported in table.4

Table 4, Magnetic moment of the complexes:

| S.N. | complex | Magnetic moment(B.M.) |
|------|---|-----------------------|
| 1. | [Mn(Fm) ₂ (SCN) ₂] | 5.80 |
| 2. | [Co(Fm) ₂ (SCN) ₂] | 4.79 |
| 3. | [Fe(Fm) ₂ (SCN) ₂] | 3.80 |
| 4. | [Cu(Fm)(SCN) ₂] | 1.90 |
| 5. | [Zn(Fm)(SCN) ₂] | diamagnetic |

Conclusion

The formazans and their transition metal complexes have a flexible structural back bone and provide opportunity to develop molecular materials of desired opto electronic as well as chromophoric compounds with wide spread applications in bio-sensors, catalytic research, photo-voltaic science and electronic materials. In the above study for the complexes $[M(\text{Fm})_2(\text{SCN})_2]$ Where, $M = \text{Co(II)} / \text{Ni(II)} / \text{Mn(II)}$, $\text{Fm} = \text{Formazan}$ octahedral geometry have been suggest while $[M(\text{Fm})_2(\text{SCN})_2]$ Where, $M = \text{Cu(II)} / \text{Zn(II)}$ probably have square planer geometry. The conclusion is based on the magnetic moment values and electronic absorptions of the complexes.

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