

Synthesis and Structural Studies of the Complexes of the Type $[\text{Fe}(\text{C}_5\text{H}_4\text{Hg})_2\text{M}(\text{NCX})_6]$ Where $\text{M}=\text{Si}(\text{IV}), \text{Sn}(\text{IV}), \text{Ti}(\text{IV}), \text{Zr}(\text{IV})$ and $\text{Hf}(\text{IV})$ and $\text{X}=\text{S}-$ OR $\text{Se}-$



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Abstract

In the case of hexathiocyanato complexes, two types of bands are present in $\nu(\text{C}-\text{N})$ region. One in the range $2155-2180 \text{ cm}^{-1}$, and the other in $2020-2025 \text{ cm}^{-1}$. The former is indicative of the presence of bridging thiocyanate, and the latter of the N-bonded terminal thiocyanate. The bands in the $\nu(\text{C}-\text{S})$ and $\delta(\text{NCS})$ region also indicate the presence of both bridging and terminal thiocyanates. The presence of both bridging and terminal thiocyanates is indicative of a structure. The spectra of the complexes have been recorded both in solid and solution phases. There is no change in the position of $\nu(\text{C}-\text{N})$ stretching frequency. This shows that the complexes are monomer.

Keywords: Hexathiocyanato, Ferrocene and Stretching Frequency.

Introduction

Tramer⁽¹⁾ first reported the metal hexathiocyanate of $\text{Pt}(\text{IV})$ and synthesized $\text{MPt}(\text{SCN})_6$, $[\text{M}=\text{Co}, \text{Pb}, \text{Hg}, \text{Zn}, \text{Cu}$ and $\text{Fe}]$. Schimitz⁽²⁾ and Bailey⁽³⁻⁴⁾ reported hexathiocyanate of the type $\text{K}_2\text{M}(\text{NCS})_6$. [where, $\text{M}=\text{Ti}(\text{IV}), \text{Zr}(\text{IV}), \text{Hf}(\text{IV}), \text{Re}(\text{IF}), \text{Pt}(\text{IV})$ and $\text{Sn}(\text{IV})$]. $[\text{M}(\text{NCS})_4(\text{bipy})_2]$ type of complexes, [where, $\text{M}=\text{Zr}(\text{IV})$ and $\text{Hf}(\text{IV})$] had been prepared and reported⁽⁵⁾. X-ray structure shows a N-bonded thiocyanate⁽⁶⁾, $[\text{K}_2\text{M}(\text{XCN})_6]$ [where, $\text{M}=\text{Si}(\text{IV}), \text{Sn}(\text{IV}), \text{Ti}(\text{IV}), \text{Zr}(\text{IV})$ and $\text{Hf}(\text{IV})$, $\text{X}=\text{S}^-$ or Se^-] have been prepared and reacted with 1,1'-bis (thiocyanato mercurio) ferrocene, a new series of complexes resulted which are presented in this chapter.

Objective of the Study

Synthesis and structural study of $[\text{Fe}(\text{C}_5\text{H}_4\text{Hg})_2\text{M}(\text{NCX})_6]$.

Review of Literature

Organometallic chemistry is of growing interest especially in the recent decades due to its wide applications in the biological and medicinal field, this application leads to a new area called bioorganometallic chemistry. Ferrocene moiety is used in bioorganometallic chemistry due to its stability, biological activity and application in organic synthesis to prepare new compounds. Also, metal complexes are used in bioorganometallic chemistry since they exhibit a wide range of biological activities against various diseases. Since the discovery of ferrocene 1 in 1951 (Kealy and Pauson, 1951), ferrocene and its derivatives have attracted the attention of many researchers in the field of organometallic chemistry for using in various applications such as materials science (Kadkin et al., 2007; Ochi et al., 2010), bio-organometallic and biological chemistry (Sudhir et al., 2010; Molina et al., 1999; Patra et al., 2010), nonlinear optics (Morales-Espinoza et al., 2010), asymmetric catalysis (Sondenecker et al., 2011), polymer science as redox active polymers (Hudson, 2001), electrochemistry (Zheng et al., 2013; Qiao et al., 2009), corrosion inhibition (Gupta et al., 2014) and molecular recognition as biosensors (Beer et al., 1992; Beer and Smith, 1998; Moore et al., 1993). Many ferrocene compounds display interesting antibacterial (Kazemizadeha et al., 2016), antifungal (Dou et al., 2008), antimalarial (Itoh et al., 2000; Kumar et al., 2014), antitumor (Hafez et al., 2013; Long et al., 2009), antioxidant (Hussain et al., 2013) and cytotoxic (Hassan et al., 2015a; Abd El-All et al., 2016) activities. Also, ferrocene compounds appeared promising in biological activities. For example, ferroquine 2 (FQ,

SR97193), is a new antimalarial (Dive and Biot, 2008). Compound 3 is a potent antifungal agent and showed 100% inhibitory ratios against *S. sclerotiorum*, *P. oryzae* and *C. cucumerinum* (Liu et al., 2008). Compound 4, 3-ferrocenoyl-1-(4-trifluoromethoxyphenyl) urea, shows a potential in vitro antitumor activity using reported method (Skehan et al., 1990) against cervical carcinoma cells (KB cells) (Chen et al., 2005) and compound 5, 1-(4-chlorophenyl)-3-ferrocenylurea, showed potential anti-HIV protease activity (Liu et al., 2012) (Figure 1). On the other hand, the biological activities of metal complexes have gained attention during the last two decades due to their diverse biomedical applications like antibacterial (Osman et al., 2012; Sakthilatha et al., 2015; Wakil et al., 2017), antifungal (Ran et al., 2011; El-Tabl et al., 2012), cytotoxicity (Osman et al., 2014; El-Seidy et al., 2013), antitumor (Chang et al., 2015; Rubino et al., 2016), antiviral (Abou-Melha et al., 2015), DNA cleavage (Kokare et al., 2017; Subbaraj et al., 2014), antimalarial (Hubin et al., 2014), antioxidant (Abdel-Monem et al., 2017; Lakshmi et al., 2011), analgesic and anti-inflammatory (Hoonur et al., 2010; 2011) activities.

Experimental

Material and Manipulations

Reagent grade solvent were purified and dried before use. $TiCl_4$, $HfCl_4$, $ZrCl_4$ and $SiCl_4$ were taken from fresh bottles. Potassium thiocyanate was vacuum dried for 12 hours before use. $[K_2M(SCN)_6]$ [where, M = Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV)] was prepared by reported method as given below:

Preparation of $[K_2Sn(NCS)_6]$

Tin tetrachloride and potassium thiocyanate was separately dissolved in acetonitrile in 250 ml round bottom flask in 2:12 molar ratio. Tin tetrachloride solution in acetonitrile was dropwise added in the stirring solution of potassium thiocyanate with the help of dropping funnel. After the complete addition of both the solutions the reaction mixture was further stirred for a period of six hours. The white precipitate of potassium chloride separates out which was filtered off and rejected. The filtrate was concentrated by vacuum evaporation and placed in a vacuum desiccators. After a few hours white mass separates out. The solvent was removed by decantation and compound was dried in vacuum. Whole procedure was carried out in strict dry conditions in an atmosphere of nitrogen. The purity of the compound was tested by elemental analysis and infrared spectral measurements. Complexes of the type $K_2M(NCS)_6$ [where, M = Zr(IV), Hf(IV), Ti(IV) and Si(IV)] were similarly prepared. The purity of the compounds was tested by analysis and infrared spectral measurements.

Physical Measurements

m.p. = 178°C
colour = White crystal.

Elemental Analysis

| | Sn% | S% | N% |
|--------------|---|-------|-------|
| Obs. | 21.26 | 35.12 | 14.24 |
| Cal. | 21.78 | 35.22 | 15.41 |
| Conductance: | 157.75 cm ⁻² mol ⁻¹ | | |

I.R. Spectral Bands

$\nu(C-N)$ = 2040(s), 1960(m)

$\nu(C-S)$ = 875(m), 860(sl)

$\delta(NCS)$ = 510(m), 483(s)

Preparation of $[Fe(C_5H_4Hg)_2 M(NCX)_6]$

[M = Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV) X = S⁻ or Se⁻]

5.45 gm (.01 mol.) of $K_2Sn(NCS)_6$ was dissolved in 100 ml of dry acetonitrile. A homogeneous suspension of 7.0 gm. (.01 mol) of 1,1'-Bis (thiocyanato) ferrocene was dissolved in same solvent in a 250 ml round bottom flask. To this suspension the solution of $K_2 Sn(NCS)_6$ was slowly added with vigorous stirring. After complete addition, the reaction mixture was refluxed for a short while, when a clear solution was obtained, turbidity if any was removed by filtration. This was stirred overnight when a precipitate of yellowish green colour obtained which was filtered, washed with the solvent and dried in vacuum. The whole procedure was carried out in strict dry condition. Other $K_2M(SCN)_6$ [M= Si(IV), Ti(IV), Zr(IV) and Hf(IV)] were similarly reacted and the respective complexes prepared yield is about 68%. The corresponding selenocyanate analogues were prepared using $K_2M(SeCN)_6$ in place of $K_2M(SCN)_6$.

All the complexes prepared are air sensitive hence whole procedure was carried out in strict dry condition in a dry box flushed with nitrogen.

Analyses of the Complexes

The complexes were, gravimetrically analysed for sulphur as barium sulphate, mercury as mercury sulphide, selenium as selenium metal⁽⁸⁾, Nitrogen by semi microkjeldahl's method. The results are included in Table 4.2.

The molar conductance was measured in dimethyl sulphoxide using a Toshniwal conductivity bridge. The infrared spectra was recorded as nujol mull on Pye Unicam sp-3-300 spectrometer in the range 4000-200 cm⁻¹. The results are presented in Table 4.3.

Results and Discussion

The complexes formed by the reaction of $K_2M(NCS)_6$ with 1,1'-Bis (thiocyanato) ferrocene with the elimination of 2 molecules of potassium thiocyanate were referred to as hexathiocyanate complexes.

The metal thiocyanate has three modes of fundamental vibration i.e. (C-N) stretching, (C-S) stretchings and (NCS) bending. The position of these bands are in the region 2000-2180 cm⁻¹, 650-860 cm⁻¹ and 400-500 cm⁻¹, respectively. The position and nature of these bands indicates the nature of thiocyanate bonding, for instance as cis octahedral has two (C-N) bands while trans has only one⁽⁹⁾. Knox and Borwn⁽¹⁰⁾ have shown the presence of six bands in the (C-N) region for hexathiocyanate of Oh symmetry e.g. $K_2M(NCS)_6$ where M = Nb(IV and V) and Ta(IV)⁽¹¹⁾. He has also shown that the number of C-N bands becomes three or four, when potassium is replaced by quaternary ion.

The position of (C-N) in N-bonded hexathiocyanate is in the range 1910-2095 cm⁻¹

whereas the corresponding range in tetrathiocyanate is narrow ($2040\text{--}2080\text{ cm}^{-1}$).

In $\text{K}_2\text{M}(\text{NCS})_6$ we observe one broad and intense band for (C–N) stretching frequency. The range of broadness is $1940\text{--}2100\text{ cm}^{-1}$. Bohland⁽¹²⁾ observe that this band is resolved into six weak bands when nujol emulsions of the sample is very much diluted. The $\nu(\text{C–S})$ region shows the presence of four bands in the region $720\text{--}860\text{ cm}^{-1}$. The number and position of these bands shows N–bonded hexathiocyanate⁽¹³⁾. The number and position of NCS bands are also very much typical of N–bonded hexathiocyanate.

When potassium of potassium hexathiocyanate was replaced by 1,1–Bis (thiocyanate mercurio) ferrocene. The number of $\nu(\text{C–N})$ bands decreases and their position changes and comes in the region ($2155\text{--}2180\text{ cm}^{-1}$) and in ($2020\text{--}2025\text{ cm}^{-1}$). The former is indicative of the presence of bridging thiocyanate, and the latter of the N–bonded terminal thiocyanate. The bands in the $\nu(\text{C–S})$ and $\delta(\text{NCS})$ region also indicate terminal thiocyanate. The presence of both bridging and terminal thiocyanates is indicative of the structure shown in the Fig. 4.1 and 4.2. The spectra of the complexes have been recorded both in solid and solution phases. There is no change in the position of

$\nu(\text{C–N})$ stretching frequency. This shows that the complexes are monomer.

Tramer⁽¹⁴⁾ also reported the infrared spectra of $\text{M}[\text{Pt}(\text{SCN})_6]$ [Me= Fe, Co, Cu, Zn, Cd] in which he shows the bridging nature of thiocyanate. In the complexes reported here, nitrogen end is linked with metal tetravalent and sulphur with mercury which is in accordance with Pearsons theory^(15–17).

The molar conductance of this series of complexes in dimethyl sulphoxide comes in the region of covalent non ionic compounds that is $21\text{--}38\text{ cm}^{-1}\text{ mol}^{-1}$.

The infrared spectra coupled with analytical and other physical measurements which shows an octahedral arrangement around M in the adducts.^(18–20) M is linked with nitrogen end of thiocyanate, having both the terminal and bridge thiocyanate. On the basis of ongoing discussion a tentative structure involving hexa co–ordination around M are presented in figure 4.1 & 4.2.

New bands at 2040s, 805m, 430s, 420ssh and 2050vs, 815m, 480s, 420scm^{-1} in the thiocyanato complexes assigned to νCN , νCS , δNCS modes are in good agreement with the presence of terminal N–bonded thiocyanato groups. In the region $1620\text{--}1233\text{ cm}^{-1}$ the ligand displays a number of bands at 1620, 1610, 1575, 1533, 1495, 1485, 1423 cm^{-1} attributed to Ferrocenyl ring skeletal vibrations.^(21–28)

Fig. 4.1
[M = Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV)]

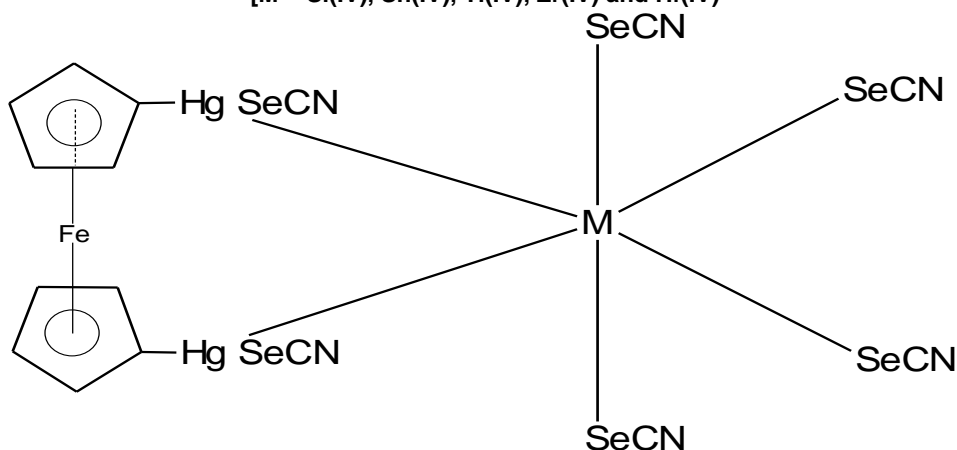


Fig. 4.2
[M = Si(IV), Sn(IV), Ti(IV), Zr(IV) and Hf(IV)]

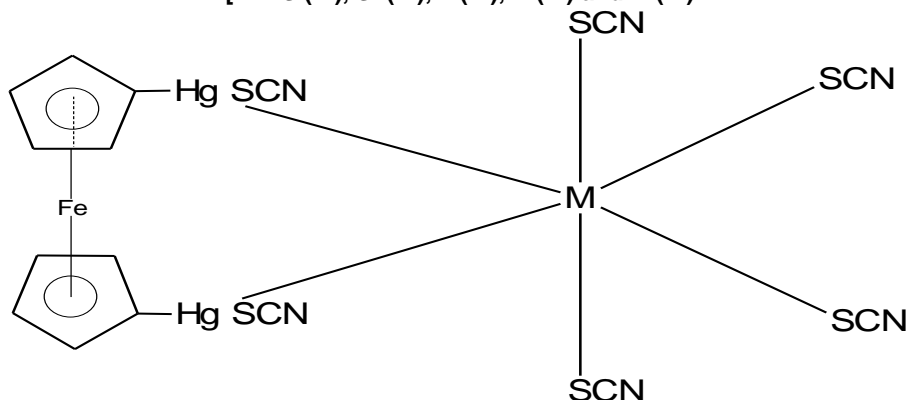


Table – 4.1
Physical Measurements

| S.No. | Complexes | Colour | Yield % | M.P. °C | ^a Molar Cond. (in DMSO cm ² mol ⁻¹) |
|-------|--|-----------------|---------|---------|---|
| 1. | [Fe(C ₅ H ₄ Hg) ₂ Si(NCS) ₆] | Cream | 60 | 182 | 32.28 |
| 2. | [Fe(C ₅ H ₄ Hg) ₂ Sn(NCS) ₆] | Yellowish green | 68 | 222 | 37.08 |
| 3. | [Fe(C ₅ H ₄ Hg) ₂ Ti(NCS) ₆] | Dirty brown | 70 | 128 | 30.15 |
| 4. | [Fe(C ₅ H ₄ Hg) ₂ Zr(NCS) ₆] | Dark green | 61 | 196 | 21.63 |
| 5. | [Fe(C ₅ H ₄ Hg) ₂ Hf(NCS) ₆] | Cream | 60 | 246 | 32.16 |
| 6. | [Fe(C ₅ H ₄ Hg) ₂ Si(NCSe) ₆] | Steel grey | 66 | 98 | 23.02 |
| 7. | [Fe(C ₅ H ₄ Hg) ₂ Sn(NCSe) ₆] | Dirty brown | 70 | 182 | 35.04 |
| 8. | [Fe(C ₅ H ₄ Hg) ₂ Ti(NCSe) ₆] | Grey | 60 | 105 | 28.26 |
| 9. | [Fe(C ₅ H ₄ Hg) ₂ Zr(NCSe) ₆] | Dirty white | 64 | 172 | 28.25 |
| 10. | [Fe(C ₅ H ₄ Hg) ₂ Hf(NCSe) ₆] | Steel grey | 62 | 194 | 24.02 |

a=decomposition

Table – 4.2
Analytical Data of the Complexes

| S.No. | Complexes | Se% | | N% | | Hg% | | M% | |
|-------|--|-------|-------|-------|------|-------|-------|-------|-------|
| | | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. |
| 1. | [Fe(C ₅ H ₄ Hg) ₂ Si(NCS) ₆] | 19.97 | 19.80 | 8.73 | 8.68 | 41.74 | 41.58 | – | – |
| 2. | [Fe(C ₅ H ₄ Hg) ₂ Sn(NCS) ₆] | 18.26 | 17.65 | 7.98 | 7.84 | 38.14 | 37.94 | 11.28 | 11.10 |
| 3. | [Fe(C ₅ H ₄ Hg) ₂ Ti(NCS) ₆] | 19.59 | 19.18 | 8.57 | 8.32 | 40.89 | 40.70 | 4.89 | 4.42 |
| 4. | [Fe(C ₅ H ₄ Hg) ₂ Zr(NCS) ₆] | 18.74 | 18.54 | 8.21 | 7.98 | 39.16 | 38.95 | 8.89 | 8.80 |
| 5. | [Fe(C ₅ H ₄ Hg) ₂ Hf(NCS) ₆] | 17.28 | 17.26 | 7.55 | 7.38 | 36.09 | 35.86 | 16.07 | 15.88 |
| 6. | [Fe(C ₅ H ₄ Hg) ₂ Si(NCSe) ₆] | 38.11 | 37.92 | 6.75 | 6.60 | 32.27 | 32.10 | 2.26 | 2.12 |
| 7. | [Fe(C ₅ H ₄ Hg) ₂ Sn(NCSe) ₆] | 35.52 | 35.40 | 6.29 | 6.15 | 30.08 | 29.90 | 8.90 | 8.70 |
| 8. | [Fe(C ₅ H ₄ Hg) ₂ Ti(NCSe) ₆] | 37.51 | 37.40 | 6.65 | 6.50 | 31.77 | 31.55 | 3.79 | 3.60 |
| 9. | [Fe(C ₅ H ₄ Hg) ₂ Zr(NCSe) ₆] | 36.72 | 36.58 | 6.43 | 6.30 | 30.71 | 30.51 | 6.98 | 6.80 |
| 10. | [Fe(C ₅ H ₄ Hg) ₂ Hf(NCSe) ₆] | 34.0 | 33.77 | 6.02 | 5.73 | 28.79 | 28.60 | 12.81 | 12.65 |

Table- 4.3

Infrared Spectral Band Assignments of the Complexes

| S.No. | Complexes | $\nu(\text{C-N})$ | $\nu(\text{C-X})$ | $\delta(\text{NCX})$ | $\delta\text{M}-(\text{NCX})$ |
|-------|--|-------------------|-------------------------|----------------------|-------------------------------|
| 1. | [Fe(C ₅ H ₄ Hg) ₂ Si(NCS) ₆] | 2180(s), 2020(sh) | 750(s), 740(sh), 770(w) | 440(s), 445(2) | 320(w) |
| 2. | [Fe(C ₅ H ₄ Hg) ₂ Sn(NCS) ₆] | 2150(s), 2025(sh) | 720(w), 710(sh) | 465(w), 450(sh) | 360(w) |
| 3. | [Fe(C ₅ H ₄ Hg) ₂ Ti(NCS) ₆] | 2140(s), 2020(sh) | 820(s), 840(w) | 420(w), 440(w) | 310(w) |
| 4. | [Fe(C ₅ H ₄ Hg) ₂ Zr(NCS) ₆] | 2125(s), 2020(sh) | 720(w) | 480(w), 440(w) | 320(w) |
| 5. | [Fe(C ₅ H ₄ Hg) ₂ Hf(NCS) ₆] | 2140(s), 2025(sh) | 725(w) | 420(w), 480(w) | 322(w) |
| 6. | [Fe(C ₅ H ₄ Hg) ₂ Si(NCSe) ₆] | 2160(s), 2020(sh) | 750(s), 740(sh), 770(w) | 465(w), 450(sh) | 267(s) |
| 7. | [Fe(C ₅ H ₄ Hg) ₂ Sn(NCSe) ₆] | 2150(s), 2025(sh) | 720(w), 710(sh) | 420(w), 440(w) | 306(s) |
| 8. | [Fe(C ₅ H ₄ Hg) ₂ Ti(NCSe) ₆] | 2140(s), 2018(sh) | 840(s), 820(s) | 480(w), 440(w) | 277(sh) |
| 9. | [Fe(C ₅ H ₄ Hg) ₂ Zr(NCSe) ₆] | 2125(s), 2020(sh) | 720(w) | 420(s) | 275(s) |
| 10. | [Fe(C ₅ H ₄ Hg) ₂ Hf(NCSe) ₆] | 2140(s), 2028(sh) | 725(w) | 480(m) | 270(m) |

s–strong; m= medium, w= weak and sh=shoulder

Conclusion

It can be concluded that ferrocenyl complexes display pharmacological and medicinal activities as antimicrobial agents against different microbes. The ferrocenyl complexes are more active than the free ligand and this activity depends on the metal ion and the tested microbes. For that, ferrocenyl complexes have attracted increasing attention of the scientists for searching of new potent pharmacological and medicinal activities.

References

1. Tramer, J. Chem. Phys. 1962, 59, pp 232, 241, 637.
2. O.Schniz and B.Ross, J. Anorg. Allg. Chem. 1966, 342, 82.
3. R.A.Bailey, T.W.Michelson and A.A.Norile, J. Inorg. Nucl. Chem. 1970, 32, 2427.
4. R.A.Bailey, S.L. Kozak, T.W. Michelson and W.N. Mills, Coord. Chem. Rev. 1976, 6, 407.
5. A.M. Goulb, T.P. Lishko, G.V. Tsintsaoze and V.V.Skopenko, Russ. J. Inorg. Chem. [Engl. Trans.] 1972, 17, 1100.
6. E.J. Peterson, R.B. Vondreele and T.M. Brown, J. Inorg. Nucl. Chem. 1976, 15, 307.
7. A.Gallart and T.M. Brown, J. Inorg. Nucl. Chem. 1972, 34, 3568.
8. A.I.Vogel, Text book of quantitative chemical analysis, Longman 1961
9. W.J.Geary, Coord. Chem. Rev. 7 (1971) 81.
10. M.M.Chamberlain & J.C.Bailar, J.Am.Chem. Soc.1959,81,6412.

11. E.G.Knox and T.M.Brown, *Inorg. Chem*; 1969, 1401.
12. R.A.Bailey, T.M.Michelson and A.A.Malik, *J. Inorg. Nucl. Chem.* 1970, 32, 2427.
13. H.Bohland, E.Tied and E.Zenker, *J. Less Common Metals* 1968, 15, 89.
14. A.Tramer, *J. Chem. Phys.* 1962, 59, 232, 637.
15. R.G.Pearson, *J. Chem. Educat.* 1968, 45, 581, 643.
16. M.Kato, T.Tanase, *Inorg. Chem.* 2005, 44, 8.
17. J.Carranza, C.Brennm, J.Sletten & J.M.Clemente Juan, *Inorg. Chem.* 2003, 42, 8716.
18. S.Mishra, L.G.H. Pfalzgraf, E.Jeanneau & H.Chermette, *Dalton Trans.* 2007, 410.
19. S.F.Si, J.K.Tang, D.Z.Liao, Z.H. Jiang & S.P.Yan, *Inorg. Chem. Commun.* 2002, 5, 76.
20. A.Mukherjee, I.Rudra, M.Nethaji, S.Ramasesha & A.R.Chakarvarti, *Inorg. Chem.* 2003, 42, 463.
21. R.S.Rarig and J.Zubieta, *Inorg. Chim. Acta* 2001, 319, 235.
22. C.Y.Su, Y.P.Cai, C.L.Chen, F.Lissner, B.S.Kang & W.Kaim, *Angew Chem. Int. Ed.* 2002, 41, 3371.
23. R.Baggio, R.Calvo, M.T.Garland, O.Pena, M.Peree & L.D.Slep, *Inorg. Chem. Commun.* 2007, 10, 1249.
24. R.Baldoma, M.Monfort, J.Ribas, X.Solans & M.A.Maestro, *Inorg. Chem.* 2006, 45, 8144.
25. D.Li, S.Li, D.Sang, J.Yu, J.Huang, Y.Li and W.Tang, *Inorg. Chem.* 2003, 42, 6071.
26. S.Youngme, G.A.Van Albada, O.Roubeau, C.Pakawatachai, N.Chaichit and J. Reedjik, *Inorg. Chim. Acta* 2003, 342, 48.
27. A.K. Das, N.S.Gowda, M.Botoshansky, M.A.Sridhar, M.Kaftory & J.S.Prasad, *J. Mol. Struct.* 2009, 938, 259.
28. C.Qiao, J.Li, Y.Xu, S.Guo, X. Qi & Y.Fan, *J. Coord. Chem.* 2009, 62, 3268.
29. Abd El-All AS, Hassan AS, Osman SA, Yosef HAA, AbdelHady WH, El-Hashash MA, Atta-Allah SR, Ali MM, El Rashedy AA. *Synthesis, characterization and biological evaluation of new fused triazine derivatives based on 6-methyl-3-thioxo-1,2,4-triazin-5-one.* *Acta Pol Pharm*, 2016; 73:79.
30. Abdel-Monem YK, Abou El-Enein SA, El-Sheikh-Amer MM. *Design of new metal complexes of 2-(3-amino-4,6-dimethyl-1Hpyrazolo[3,4-b]pyridin-1-yl)aceto-hydrazide: Synthesis, characterization, modelling and antioxidant activity.* *J Mol Struct*, 2017; 1127:386.
31. Abou-Melha K, Refat MS, Sadik A. *A series of taurocholic acid complexes, spectral, kinetic, molecular modeling, and antiviral activity studies.* *Synth React Inorg Met Org Chem*, 2015; 45:884.
32. Beer PD, Nation JE, Harman ME, Hursthouse MB. *Synthesis, electrochemistry and complexation studies of new redox active bisferrocene acyclic and macrocyclic thioethers.* *J Organomet Chem*, 1992; 441:465.
33. Beer PD, Smith DRJ. *Tunable bis(ferrocenyl) receptors for the solution-phase electrochemical sensing of transition-metal cations.* *J Chem Soc Dalton Trans*, 1998; 3:417.
34. Chang H-Q, Jia L, Xu J, Xu Z-Q, Chen R-H, Wu W-N, Bie H-Y, Zhu T-F, Ma T-I, Wang Y. *Syntheses, characterizations, antitumor activities and cell apoptosis induction of Cu(II), Zn(II) and Cd(II) complexes with hydrazone Schiff base derived from isonicotinohydrazide.* *Inorg Chem Commun*, 2015; 57:8.
35. Chen L, Wang Q, Huang R, Mao C, Shang J, Song H. *Synthesis of ferrocenylphenylureas and the crystal structure of FcCONHCONHC6 H5 .* *Appl. Organometal Chem*, 2005; 19:45
36. Dive D, Biot C. *Ferrocene conjugates of chloroquine and other antimalarials: the development of ferroquine, a new antimalarial.* *Chem Med Chem*, 2008; 3:383.
37. Dou Y-Y, Xie Y-F, Tang L-F. *Synthesis, electrochemical properties and fungicidal activity of 1,1'-bis(aryl)ferrocenes and their derivatives.* *Appl Organometal Chem*, 2008; 22:25
38. El-Seidy AMA, El-Zahany E, Barakat AS, Youssef NS, Galal SA, Drweesh SA. *Synthesis, characterization, and cytotoxic activity on MCF-7 cell line of some novel metal complexes with substituted benzimidazole ligands.* *Synth React Inorg Met Org Chem*, 2013; 43:46.
39. El-Tabl AS, Shakhofa MME, El-Seidy AMA, Al-Hakimi AN. *Synthesis, characterization and antifungal activity of metal complexes of 2-(5-(2-chlorophenyl)diazonyl)-2-hydroxybenzylidene) hydrazinecarbothioamide.* *Phosphorus Sulfur and Silicon and the Related Elements*, 2012; 187:1312.
40. Gupta SR, Mourya P, Singh MM, Singh VP. *Synthesis, structural, electrochemical and corrosion inhibition properties of two new ferrocene Schiff bases derived from hydrazides.* *J Organomet Chem*, 2014; 767:136.
41. Hafez TS, Osman SA, Yosef HAA, Abd El-All AS, Hassan AS, El-Sawy AA, Abdallah MM, Youns M. *Synthesis, structural elucidation and in vitro antitumor activities of some pyrazolopyrimidines and Schiff bases derived from 5-amino-3-(arylamino)-1H-pyrazole-4-carboxamides.* *Sci Pharm*, 2013; 81:339.
42. Hassan AS, Hafez TS, Osman SA, Ali MM. *Synthesis and in vitro cytotoxic activity of novel pyrazolo[1,5-a]pyrimidines and related Schiff bases.* *Turk J Chem*, 2015a; 39:1102.
43. Hoonur RS, Patil BR, Badiger DS, Vadavi RS, Gudasi KB, Chandrashekhar VM, Muchchandi IS. *Synthesis, characterization, antiinflammatory and analgesic activity of transitionmetal complexes of 3-[1-(2-hydroxyphenyl)ethylidamino]-2-phenyl-3,4-dihydroquinazolin-4(3H)-one.* *Appl Organometal Chem*, 2011; 25:476.
44. Hoonur RS, Patil BR, Badiger DS, Vadavi RS, Gudasi KB, Dandawate PR, Ghaisas MM, Padhye SB, Nethaji M. *Transition metal complexes of 3-aryl-2-substituted 1,2-dihydroquinazolin-4(3H)-one derivatives: New class of analgesic and anti-inflammatory agents.* *Eur J Med Chem*, 2010; 45:2277.
45. Hubin TJ, Amoyaw PNA, Roewe KD, Simpson NC, Maples RD, Freeman TNC, Cain AN, Le JG,

- Archibald SJ, Khan SI, Tekwani BL, Khan MOF. Synthesis and antimalarial activity of metal complexes of crossbridged tetraazamacrocyclic ligands. *Bioorg Med Chem*, 2014; 22:3239.
46. Hudson RDA. Ferrocene polymers: current architectures, syntheses and utility. *J Organomet Chem*, 2001; 637:47.
 47. Hussain RA, Badshah A, Sohail M, Lal B, Altaf AA. Synthesis, chemical characterization, DNA interaction and antioxidant studies of ortho, meta and para fluoro substituted ferrocene incorporated selenoureas. *Inorg Chim Acta*, 2013; 402:133.
 48. Itoh T, Shirakami S, Ishida N, Yamashita Y, Yoshida T, Kim H-S, Wataya Y. Synthesis of novel ferrocenyl sugars and their antimalarial activities. *Bioorg Med Chem Lett*, 2000; 10:1657.
 49. Kadkin ON, Han H, Galyametdinov YG. Synthesis, computational modelling and liquid crystalline properties of some [3] ferrocenophane-containing Schiff's bases and β -aminovinylketone: Molecular geometry-phase behaviour relationship. *J Organomet Chem*, 2007; 692:5571.
 50. Kazemizadeha AR, Shajari N, Shapouri R, Adibpour N, Teimuri-Mofradd R, Dinmohammadi P. One-pot, four-component synthesis of 1,3,4-oxadiazole derivatives containing a ferrocene unit and their antimicrobial activity. *Appl Organometal Chem*, 2016; 30:148.
 51. Kealy TJ, Pauson PL. A new type of organo-iron compound. *Nature*, 1951; 168:1039.
 52. Kokare DG, Kamat V, Naik K, Nevrekar A, Kotian A, Revankar VK. Evaluation of DNA cleavage, antimicrobial and anti-tubercular activities of potentially active transition metal complexes derived from 2,6-di(benzofuran-2-carbohydrazono)-4-methylphenol. *J Mol Struct*, 2017; 1127:289.
 53. Kumar K, Pradines B, Madamet M, Amalvict R, Benoit N, Kumar V. 1H-1,2,3-triazole tethered isatin-ferrocene conjugates: Synthesis and in vitro antimalarial evaluation. *Eur J Med Chem*, 2014; 87:801.
 54. Lakshmi GC, Ananda S, Gowda NMM. Synthesis, characterization, and antioxidant activity evaluation of pyridoxine and its transition metal complexes. *Synth React Inorg Met Org Chem*, 2011; 41:413.
 55. Liu W, Tang Y, Guo Y, Sun Bo, Zhu H, Xiao Y, Dong D, Yang C. Synthesis, characterization and bioactivity determination of ferrocenyl urea derivatives. *Appl Organometal Chem*, 2012; 26:189.
 56. Liu Y-T, Lian G-D, Yin D-W, Su B-J. Synthesis, characterization and biological activity of ferrocene-based Schiff base ligands and their metal (II) complexes. *Spectrochimica Acta Part A*, 2013; 100:131.
 57. Liu J, Li L, Dai H, Fang J. Synthesis and biological activities of new 1H-1,2,4-triazole alcohol derivatives containing a ferrocenyl moiety. *Appl Organometal Chem*, 2008; 22:237.
 - Long B, Liang S, Xin D, Yang Y, Xiang J. Synthesis, characterization and in vitro antiproliferative activities of new 13-cisretinoyl ferrocene derivatives. *Eur J Med Chem*, 2009; 44:2572.
 58. Molina P, Tarraga A, Lopez JL, Martinez JC. Preparation and heterocyclization reactions of ferrocenylazido ketones. Useful buildingblocks for the synthesis of ferrocenyl-substituted azaheterocycles. *J Organomet Chem*, 1999; 584:147.
 59. Moore AJ, Skabara PJ, Bryce MR, Batsanov AS, Howard JAK, Daley STAK. Covalently attached ferrocene and tetrathiafulvalene redox systems. *J Chem Soc Chem Commun*, 1993; 4:417.
 60. Morales-Espinoza EG, Sanchez-Montes KE, Klimova E, Klimova T, Lijanov IV, Maldonado JL, Ramos-Ortiz G, Hernandez-Ortega S, Martinez-Garcia M. dendrimers containing ferrocene and porphyrin moieties: synthesis and cubic non-linear optical behavior. *Molecules*, 2010; 15:2564.
 61. Ochi Y, Suzuki M, Imaoka T, Murata M, Nishihara H, Einaga Y, Yamamoto K. controlled storage of ferrocene derivatives as redox-active molecules in dendrimers. *J Am Chem Soc*, 2010; 132:5061.
 62. Osman SA, Mousa HA, Yosef HAA, Hafez TS, El-Sawy AA, Abdallah MM, Hassan AS. Synthesis, characterization and cytotoxicity of mixed ligand Mn(II), Co(II) and Ni(II) complexes. *J Serb Chem Soc*, 2014; 79:953.
 63. Osman SA, Yosef HAA, Hafez TS, El-Sawy AA, Mousa HA, Hassan AS. Synthesis and antibacterial activity of some novel chalcones, pyrazoline and 3-cyanopyridine derivatives based on khellinone as well as Ni(II), Co(II) and Zn(II) complexes. *Aust J Basic Appl Sci*, 2012; 6:852.
 64. Patra M, Gasser G, Wenzel M, Merz K, Bandow JE, MetzlerNolte N. Synthesis and biological evaluation of ferrocene-containing bioorganometallics inspired by the antibiotic platensimycin lead structure. *Organometallics*, 2010; 29:4312.
 65. Qiao C, Li J, Xu Y, Guo S, Qi X, Fan Y. Synthesis, structural characterization and electrochemical recognition of metal ions of two new ferrocenylhydrazone-based receptors. *Appl Organometal. Chem*, 2009; 23:421.
 66. Ran X, Wang L, Cao D, Lin Y, Hao J. Synthesis, characterization and in vitro biological activity of cobalt(II), copper(II) and zinc(II) Schiff base complexes derived from salicylaldehyde and D,L-selenomethionine. *Appl Organometal Chem*, 2011; 25:9.
 67. Rubino S, Pibiri I, Costantino C, Buscemi S, Girasolo MA, Attanzio A, Tesoriere L. Synthesis of platinum complexes with 2-(5-perfluoroalkyl-1,2,4-oxadiazol-3-yl)-pyridine and 2-(3-perfluoroalkyl-1-methyl-1,2,4-triazole-5-yl)-pyridine ligands and their in vitro antitumor activity. *J Inorg Biochem*, 2016; 155:92.
 68. Sakthilatha D, Deepa A, Rajavel R. Spectroscopic characterization and in vitro antibacterial activity of some novel metal complexes with Schiff base ligands derived from

- thiosemicarbazide. *Synth React Inorg Met Org Chem*, 2015; 45:286.
69. Skehan P, Storeng R, Scudiero D, Monks A, McMahon J, Vistica D, Warren JT, Bokesch H, Kenney S, Boyd MR. New colorimetric cytotoxicity assay for anticancer-drug screening. *J Natl Cancer Inst*, 1990; 24:1107-1112.
70. Sondenecker A, Cvengros J, Aardoom R, Togni A, Stereogenic P. Ferrocene-based (trifluoromethyl) phosphanes: synthesis, structure, coordination properties and catalysis. *Eur J Org Chem*, 2011; 2011:78.
71. Subbaraj P, Ramu A, Raman N, Dharmaraja J. Synthesis, characterization, and pharmacological aspects of metal(II) complexes incorporating 4-[phenyl(phenylimino)methyl]benzene-1,3-diol. *J Coord Chem*, 2014; 67:2747.
72. Sudhir VS, Kumar NYP, Chandrasekaran S. Click chemistry inspired synthesis of ferrocene amino acids and other derivatives. *Tetrahedron*, 2010; 66:1327.
73. Wakil IM, Ndahi NP, Abubakar MB, Waziri I. Synthesis, Characterization, and Antimicrobial Studies of Propionaldehyde Schiff base Metal (II) Complexes. *Chem Res J*, 2017; 2:39.
74. Zheng J, Wu KL, Shi TH, Xu Y. A series of novel ferrocenebased dipeptide receptors for electrochemistry and biological activity. *Appl Organometal Chem*, 2013; 27:698.