Chapter 4

SYNTHESIS OF COMPLEXES

This chapter describes experimental details of complexes of Ni\textsuperscript{II}, Pd\textsuperscript{II}, Cu\textsuperscript{I,II} and Co\textsuperscript{III} metal ions with a series of thiosemicarbazone ligands (Chapter 3) in the absence or presence of co-ligands (Chart 4, Chapter 2). Complexes have been characterized by the analytical data, spectroscopic techniques and single crystal X-ray crystallography.

A series of thiosemicarbazone ligands (H\textsubscript{n}L) have been used in this project. In all the complexes synthesized, the thiosemicarbazone ligands (H\textsubscript{n}L) are binding as anionic thiosemicarbazonates (uninegative or dinegative). The uninegative form of all the ligands (L\textsuperscript{−}, HL\textsuperscript{−}) refers to the anion formed after the deprotonation of hydrazinic (-N\textsubscript{2}H-) group (n = 1, HL; 2, H\textsubscript{2}L). The ligands (H\textsubscript{2}L) form dinegative anions (L\textsuperscript{2−}) after the loss of an additional proton from the R\textsubscript{1} group at C\textsubscript{2} carbon such as -OH (hydroxyphenyl), -N\textsubscript{4}H- (pyrrole) or C–H (phenyl, thiophene). In case of copper(I) complexes, thio- ligands generally coordinated in neutral form.

4.1 General Procedures

The interactions of metal(II) salts with a series of N\textsuperscript{1}- substituted thiosemicarbazones (Chapter 3) in the presence or absence of co-ligands (Chart 4, Chapter 2) have been carried out. Seven broad procedures were adopted for preparing metal complexes (details of complexes with numbering follows general procedure).

Method 1

In this method, thio- ligand was dissolved in methanol (10 mL) and to it was added solid nickel(II) acetate in 1 : 2 molar ratio (M : L). Upon stirring for a period of 4 h, clear solution was formed. Slow evaporation of the resulting solution yielded a complex. Complexes 1–17 have been prepared by this method. A representative reaction is given below:
Method 2

To a solution of thiosemicarbazone ($\text{H}_2\text{L}$, with 2-hydroxyphenyl based) in methanol (15 mL) was added solid Ni(OAc)$_2$ / Cu(OAc)$_2$. The contents were stirred for a period of 2 h, which resulted in the formation of rust colored precipitates. These precipitates have very low solubility. The analytical data supported the formation of compound of empirical composition, {ML} (M = Ni, Cu). The addition of co-ligands to the suspension of {ML} in CH$_3$CN resulted in the formation of a clear solution. Complexes 19, 20, 23–39, 41–49, 55 and 65–72 have been prepared by this method. Crystals for X-ray were grown either directly from the clear solution obtained after the addition of co-ligand or by the crystallization of the solid obtained after the evaporation of the solution. Equation indicating synthesis of complex 19 is given below:

$$\text{Ni(OAc)}_2 + \text{H}_2\text{stscN-Me} \xrightarrow{\text{methanol, stirring}} \{\text{Ni(stscN-Me)}\} \xrightarrow{\text{py, acetonitrile, stirring}} [\text{Ni(stscN-Me)(py)}]$$

Method 3

It may be noted that the addition of PPh$_3$ to the suspension of {NiL} in CH$_3$CN did not give a clear solution. So the reactions were performed with NiCl$_2$ salt. Reaction of NiCl$_2$ salt dissolved in acetonitrile with thiosemicarbazone in 1 : 1 molar ratio (M : L) in the presence of Et$_3$N base (1mL) under stirring for 4h, resulted in the formation of rust colored precipitates. The addition of P- donor coligands (PPh$_3$, dppe) to these precipitates dissolved the precipitates completely. Slow evaporation of the resulting solution gave complexes 21, 22 and 50–52.

$$\text{NiCl}_2 + \text{H}_2\text{stscN-Me} \xrightarrow{\text{Et}_3\text{N, PPh}_3, \text{acetonitrile, stirring}} [\text{Ni(stscN-Me)(PPh}_3)] + \text{Et}_3\text{NH}^+\text{Cl}^-$$

Method 4

In this method thio- ligand was dissolved in acetonitrile (10 mL) and to it solid Ni(OAc)$_2$ was added. During stirring period of 1 h, rust colored precipitates were formed. To these ppt was added a co-ligand and the contents were stirred till a clear solution was obtained. Complexes 40, 53 and 54 were prepared by this method.

$$\text{Ni(OAc)}_2 + \text{H}_2\text{stscN-Me} \xrightarrow{1/2 \text{phen, acetonitrile, stirring}} [\text{Ni}_2\text{(stscN-Me)}_2(\text{phen})(\text{OH}_2)]\cdot\text{CH}_3\text{COOH}$$
Method 5

Reactions of the precursor PdCl$_2$(PPh$_3$)$_2$ with thio- ligands in 1 : 1 molar ratio (M : L) in the presence of Et$_3$N base, in toluene or acetonitrile resulted in separation of white Et$_3$NH$^+$Cl$^-$ salt along with formation of clear red or yellow solution. Evaporation of the solution resulted in the formation of products 56–64. A representative reaction is given below:

\[
PdCl_2(PPh_3)_2 + H_2attscN-Me \xrightarrow{\text{toluene, Et}_3N} [Pd(attscN-Me)(PPh_3)] \quad (56)
\]

Method 6

In this method, thio- ligand was dissolved in methanol and solid copper(II) chloride was added to it. Green precipitates were formed during stirring. Refluxing of these contents yielded a crystalline compound. Complexes 73–75 have been prepared by this method.

\[
CuCl_2 + 2 HttscN-Me \xrightarrow{\text{methanol, stirring}} [CuCl(HttscN-Me)_2] \quad (73)
\]

Method 7

Reactions of CoCl$_2$·6H$_2$O with HttscN-Me in 1:3 molar ratio in the presence of Et$_3$N base, under refluxing resulted in separation of white Et$_3$NH$^+$Cl$^-$ salt along with formation of complex 76. Complex 77 has been prepared similarly.

\[
CoCl_2 + 3 HttscN-Me \xrightarrow{\text{toluene, Et}_3N} [Co(ttscN-Me)_3] \quad (76)
\]

4.2 Experimental Details

\[\text{[Ni}(\kappa^2-N^3,S-\text{ftscN-Me})_2] \quad (I)\]

To a light brown solution of HftscN-Me (0.036 g, 0.200 mmol) in methanol (10 mL) was added solid Ni(OAc)$_2$ (0.025 g, 0.100 mmol). The color the solution changed to reddish brown and it was stirred for about 4 h. The clear solution after filtration was left for crystallization. During slow evaporation of the solution, red compound was
separated, which was crystallized in dichloromethane and methanol mixture (3:1 :: v/v). Color: red (77%, M.p. 248–250 °C). Anal. Calcd. for C₁₄H₁₆N₆NiO₂S₂: C, 39.74; H, 3.81; N, 19.87 %; Found: C, 39.52; H, 3.52; N, 19.81 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3378br; ν(C–H) 3053m, 2925m, 2881m; ν(C=N) + ν(C=C) 1522s, 1514s; ν(C–N) 1064s, 1027s, 944s; ν(C–S) 771s. ¹H NMR (δ, ppm; CDCl₃): = 7.69 (2H, s, C²H), 7.51 (2H, d, C⁶H), 7.41 (2H, d, C⁴H), 6.98 (2H, d, N¹H), 2.91 (6H, d, CH₃) ppm. Electronic absorption spectrum (10⁻⁴ M in CH₂Cl₂, λₘₐₓ/nm, ε/L mol⁻¹ cm⁻¹): 430 (0.80 × 10⁴), 375 (1.65 × 10⁴), 325 (1.80 × 10⁴), 270 (1.75 × 10⁴).

[Ni(κ²-N₃S-ftscN-Et)] (2)

It was prepared by a method similar to that for complex 1. Color: brown (76%, M.p. 210–212 °C). Anal. Calcd. for C₁₆H₂₀N₆NiO₂S₂: C, 42.60; H, 4.44; N, 18.64 %; Found: C, 42.51; H, 4.90; N, 19.09 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3381br; ν(C–H) 3034m, 2926m, 2890m; ν(C=N) + ν(C=C) 1522s, 1508s; ν(C–N) 1085s, 1049s, 947s; ν(C–S) 764s. ¹H NMR (δ, ppm; CDCl₃): = 7.45 (4H, d, C²H + C⁶H), 7.38 (2H, d, C⁴H), 6.51 (2H, m, C⁵H), 4.98 (2H, sb, N¹H), 3.38 (4H, m, CH₂), 1.25 (6H, t, CH₃) ppm. Electronic absorption spectrum (10⁻⁴ M in CH₂Cl₂, λₘₐₓ/nm, ε/L mol⁻¹ cm⁻¹): 425 (0.80 × 10⁴), 377 (1.80 × 10⁴), 321 (2.03 × 10⁴), 261 (1.91 × 10⁴).

[Ni(κ²-N₃,S-ftscN-Ph)] (3)

It was prepared by a method similar to that for complex 1. Color: black (74%, M.p. 225–227 °C). Anal. Calcd. for C₂₄H₂₀N₆NiO₂S₂: C, 52.67; H, 3.66; N, 15.36 %; Found: C, 52.68; H, 3.93; N, 15.59 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3360s; ν(C–H) 3056m, 2970m; ν(C=N) + ν(C=C) 1530s, 1510s; ν(C–N) 1088s, 1047s, 889s; ν(C–S) 755s. ¹H NMR (δ, ppm; CDCl₃): δ = 7.11 (2H, t, N¹H), 7.55 (2H, s, C²H), 7.48 (8H, m, C⁶H + o- + p-Hₚₘ), 7.34 (4H, m, m-Hₚₘ), 6.86 (2H, s, C⁴H), 6.46 (2H, q, C⁵H) ppm. Electronic absorption spectrum (10⁻⁴ M in CH₂Cl₂, λₘₐₓ/nm, ε/L mol⁻¹ cm⁻¹): 420m (0.60 × 10⁴), 373 (1.52 × 10⁴), 343 (1.67 × 10⁴), 258 (2.02 × 10⁴).
[**Ni(κ²-N³,S-ttscN-Me)₂**] (4)

It was prepared by a method similar to that for complex **I**. Color: brown (73%, M.p. 255–257 °C). Anal. Calcd. for C₁₄H₁₆N₆NiS₄: C, 36.94; H, 3.51; N, 18.47 %; Found: C, 36.91; H, 3.58; N, 18.76 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3358br; ν(C–H) 2986m, 2925m, 2861m; ν(C=N) + ν(C=C) 1522s, 1508s; ν(C–N) 1090s, 1003s, 948s; ν(C–S) 754s. 

**¹H NMR (δ, ppm; CDCl₃):** δ = 8.18 (2H, s, C²H), 7.47 (4H, m, C⁴H + C⁶H), 7.06 (2H, d, C⁵H), 5.05 (2H, sb, N¹H), 3.26 (6H, d, CH₃) ppm. Electronic absorption spectrum (10⁻⁴ M in CH₂Cl₂, λₘₐₓ/νₘₐₓ, ε/L mol⁻¹ cm⁻¹): 430 (0.61 × 10⁴), 376 (2.65 × 10⁴), 315 (2.01 × 10⁴), 270 (0.80 × 10⁴).

[**Ni(κ²-N³,S-ttscN-Et)₂**] (5)

It was prepared by a method similar to that for complex **I**. Color: black (75%, M.p. 194–196 °C). Anal. Calcd. for C₁₆H₂₀N₆NiS₄: C, 39.17; H, 4.14; N, 17.40 %; Found: C, 39.01; H, 4.39; N, 16.99 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3363br; ν(C–H) 3038m, 2980m, 2888m, 2828w; ν(C=N) + ν(C=C) 1522s, 1506s; ν(C–N) 1050s, 1041s, 874s; ν(C–S) 778s. 

**¹H NMR (δ, ppm; CDCl₃):** δ = 7.06 (2H, s, C²H), 6.98 (2H, s, C⁶H), 6.79 (2H, sb, N¹H), 6.51 (2H, s, C⁴H), 6.20 (2H, d, C⁵H), 3.09 (4H, m, CH₂), 1.37 (6H, t, CH₃) ppm. Electronic absorption spectrum (10⁻⁴ M in CH₂Cl₂, λₘₐₓ/νₘₐₓ, ε/L mol⁻¹ cm⁻¹): 420 (0.51 × 10⁴), 374 (1.74 × 10⁴), 318 (1.93 × 10⁴), 252 (1.78 × 10⁴).

[**Ni(κ²-N³,S-ttscN-Ph)₂**] (6)

It was prepared by a method similar to that for complex **I**. Color: yellow (77%, M.p. 188–190 °C). Anal. Calcd. for C₂₄H₂₀N₆NiS₄: C, 49.71; H, 3.45; N, 14.50 %; Found: C, 50.06; H, 3.92; N, 14.34 %. IR (KBr, cm⁻¹, selected...
absorption bands): v(N\textsuperscript{1}–H) 3414br; v(C–H), 3024m, 2996m; v(C=N) + v(C=C) 1545s, 1506s; v(C–N) 1060s, 1029s, 883s; v(C–S) 750s.

\[ \text{[Ni(κ²-N₃,S-HptscN-Ph)₂] (7)} \]

It was prepared by a method similar to that for complex \( I \). Color: brown (71%, M.p. 226–230 °C). Anal. Calcd. for C\textsubscript{24}H\textsubscript{22}N\textsubscript{8}NiS\textsubscript{2}: C, 52.81; H, 4.03; N, 20.54 %; Found: C, 52.97; H, 4.27; N, 20.62 %.

IR (KBr, cm\textsuperscript{-1}, selected absorption bands): v(N\textsuperscript{1}–H) 3428br; v(N\textsuperscript{4}–H) 3316s; v(C–H), 3061m, 2995m; v(C=N) + v(C=C) 1598s, 1542s; v(C–N) 1020s; v(C–S) 750s.

\[ \text{[Ni(κ³-N₃,N₃,S-pytscN-Me)₂]·H₂O (8)} \]

To a suspension of HpytscN-Me ligand (0.039 g, 0.200 mmol) in acetonitrile (10 mL) was added solid Ni(OAc)\textsubscript{2} salt (0.025 g, 0.100 mmol). The color of the solution changed to red and it was refluxed for 5 h. The red compound was separated during refluxing which was crystallized from acetonitrile and dichloromethane (3:1 :: v/v). Color: red (56%, M.p. 292–294 °C). Anal. Calcd. for C\textsubscript{16}H\textsubscript{20}NiN\textsubscript{8}S\textsubscript{2}O: C, 41.45; H, 4.32; N, 24.18 %; Found: C, 41.87; H, 4.08; N, 24.40 %. IR (KBr, cm\textsuperscript{-1}, selected absorption bands): v(N\textsuperscript{1}–H) 3393br; v(C–H) 3015w, 2928w, 2878w; v(C=N) + v(C=C) 1601s, 1514s; v(C–N) 1099s, 1038s; v(C–S) 767s. Electronic absorption spectrum (10\textsuperscript{-4} M in CH\textsubscript{3}OH, \( \lambda_{\text{max}}/\text{nm}, \varepsilon/\text{L mol}^{-1}\text{cm}^{-1} \)): 800 (50, 10\textsuperscript{-3} M) 402 (1.36 \times 10\textsuperscript{4}), 362 (1.60 \times 10\textsuperscript{4}), 345 (1.62 \times 10\textsuperscript{4}), 301 (1.52 \times 10\textsuperscript{4}), 224 (1.76 \times 10\textsuperscript{4}). Magnetic moment, \( \mu_{\text{eff}} = 2.98 \) BM.
[Ni(κ³-N⁴,N³,S-pytsC-N-Et)₂] (9)

It was prepared by a method similar to that for complex 8. Color: dark brown (59%, M.p. above 300 °C). Anal. Calcd. for C₁₈H₂₂N₈NiS₂: C, 45.64; H, 4.65; N, 23.67 %. Found: C, 45.59; H, 5.01; N, 23.75 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3388br; ν(C–H) 3053w, 2974w, 2928w, 2868w; ν(C=N) + ν(C=C) 1601s, 1510s; ν(C–N) 1087s, 1047s, 923w; ν(C–S) 768s. Electronic absorption spectrum (10⁻⁴ M in CH₃OH, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 800 (50, 10⁻³ M), 407 (1.56 × 10⁴), 359 (1.47 × 10⁴), 342 (1.95 × 10⁴), 301 (1.77 × 10⁴), 226 (1.92 × 10⁴). Magnetic moment, μ_eff = 3.02 BM.

[Ni(κ³-N⁴,N³,S-pytsC-N-Ph)₂] (10)

It was prepared by a method similar to that for complex 8. Color: red (61%, M.p. above 300 °C). Anal. Calcd for C₂₆H₂₂N₈NiS₂: C, 54.81; H, 3.86; N, 19.67 %. Found: C, 54.65; H, 4.18; N, 19.51 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3393br; ν(C–H) 3055w, 3022w; ν(C=N) + ν(C=C) 1589s, 1518s; ν(C–N), 1128s, 1028w; ν(C–S) 753s. Electronic absorption spectrum (10⁻⁴ M in DMSO, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 800 (34, 10⁻³ M), 420 (0.40 × 10⁴), 375 (0.79 × 10⁴), 320 (0.50 × 10⁴), 225 (0.72 × 10⁴), 209 (0.58 × 10⁴). Magnetic moment, μ_eff = 3.13 BM.

[Ni(κ²-N³,S-btsC-N-Me)₂] (11)

To a colorless solution of HbtsC-N-Me (0.038 g, 0.200 mmol) in methanol (10 mL) was added solid Ni(OAc)₂ (0.025 g, 0.100 mmol). The color the solution changed to dark red and it was stirred for about 4 h. The clear solution after filtration was left for crystallization. Slow evaporation

**Anal. Calcd. for C₁₈H₂₀N₆NiS₂:** C, 48.73; H, 4.51; N, 18.95 %; Found: C, 48.54; H, 4.33; N, 19.01 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3387br; ν(C–H), 2987m, 2876m; ν(C=N) + ν(C=C) 1548s, 1497s; ν(C=N) 1067s, 1013s, 875s; ν(C=S) 768s. ¹H NMR (δ, ppm; CDCl₃): δ = 8.05 (4H, q, C²H + C⁴H), 7.45 (2H, s, C⁸H), 7.37 (6H, m, C⁵H + C⁷H + C⁶H), 5.03 (2H, sb, N¹H), 3.00 (6H, d, CH₃) ppm.

**[Ni(κ²-N₃,S-btscN-Ph)₂]** (12)

It was prepared by a method similar to that for complex 11. Color: brown (73%, M.p. 200–212 °C). Anal. Calcd. for C₂₈H₂₄N₆NiS₂: C, 59.22; H, 4.23; N, 14.81 %; Found: C, 58.99; H, 4.35; N, 14.95 %. IR (KBr, cm⁻¹, selected absorption bands): ν(-N¹–H) 3398br; ν(C–H) 3012m, 2998m; ν(C=N) + ν(C=C) 1545s, 1478s; ν(C=N) 1058s, 1017s; ν(C=S) 771s. ¹H NMR (δ, ppm; CDCl₃): δ = 8.01 (4H, d, C²H + C⁴H), 7.61 (2H, s, C⁸H), 7.35 (14H, m, C⁵H + C⁷H + o- + p- + m-H₆Ph), 7.09 (2H, t, C⁶H), 6.89 (2H, sb, N¹H) ppm.

**[Ni(κ³-O₃,N₃,S-aftscN-Me)₂]** (13)

To a light yellow solution of the HaftscN-Me ligand (0.039 g, 0.200 mmol) in methanol (10 mL) was added solid Ni(OAc)₂ (0.025 g, 0.100 mmol). The color of the solution changed to dark brown and it was stirred for about 4 h. The clear solution after filtration was left for crystallization. During slow evaporation of the solution, brown colored compound was separated, which was crystallized in dichloromethane and methanol mixture (3:1 :: v/v). Color: brown (75 %, M.p. 220–222 °C). Anal. Calcd. for C₁₆H₂₀N₆NiO₂S₂: C, 42.55; H, 4.43; N, 18.62 %. Found: C, 42.38; H, 4.65; N, 18.46 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3367br; ν(C–H) 3057m, 2942m, 2873m; ν(C=N) + ν(C=C) 1558s, 1541s; ν(C=S) 737s. Electronic absorption spectrum (10⁻⁴ M in CH₃OH, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 982 (540), 671 (510), 406 (2.37 × 10⁴), 331 (1.99 × 10⁴), 301 (2.09 × 10⁴), 247
(1.95×10⁴). ¹H NMR (δ, ppm; CDCl₃ + DMSO-d₆): δ = 31.86 (2H, s, C⁶H), 19.58 (2H, s, C⁴H), 17.64 (2H, s, C⁵H), 6.76 (6H, s, CH₂(C²)), 6.48 (6H, s, CH₃(N¹)), -4.09 (2H, s, N¹H) ppm. Magnetic moment: μₚ = 2.98 BM.

\[ \text{[Ni(N₃-O₃,S-aftscN-Et)] (I4)} \]

It was prepared by a method similar to that for complex I3. Color: brown (76%, M.p. 228–230 °C). Anal. Calcd. for C₁₈H₂₄N₆NiO₂S₂: C, 45.07; H, 5.01; N, 17.53%. Found: C, 45.12; H, 4.98; N, 17.54%. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3372br; ν(C–H) 3081m, 2965m, 2877m; (C=N) + (C=C) 1558s, 1507s; (C–N) 1065s, 1021s, 916s; (C–S) 735s. Electronic absorption spectrum (10⁻⁴ M in CH₃OH, λmax/µm, ε/L mol⁻¹ cm⁻¹): 983 (410), 675 (380), 405 (2.37×10⁴), 331 (1.99×10⁴), 301 (2.09×10⁴), 248 (1.95×10⁴). ¹H NMR (δ, ppm; CDCl₃ + DMSO-d₆): δ = 29.38 (2H, s, C⁶H), 18.04 (2H, s, C⁴H), 16.64 (2H, s, C⁵H), 5.02 (10H, s, CH₃(C₂) + CH₂(N¹)), 3.94 (6H, s, CH₃(N¹)), -3.01 (2H, s, N¹H) ppm. Magnetic moment: μₚ = 2.96 BM.

\[ \text{[Ni(N₃-O₃,S-aftscN-Ph)] (I5)} \]

It was prepared by a method similar to that for complex I3. Color: black (77%, M.p. 234–236 °C). Anal. Calcd. for C₂₆H₂₄N₆NiO₂S₂: C, 54.23; H, 4.17; N, 14.60%. Found: C, 54.56; H, 4.78; N, 14.40%. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3394br; ν(C–H) 3045m, 3023m; (C=N) + (C=C) 1554s, 1520s; (C–N) 1085s, 1023m, 917s; (C–S) 731s. Electronic absorption spectrum (10⁻⁴ M in CH₃OH, λmax/µm, ε/L mol⁻¹ cm⁻¹): 986 (390), 678 (350), 408 (2.39×10⁴), 330 (1.98×10⁴), 301 (2.09×10⁴), 248 (1.94×10⁴). ¹H NMR (δ, ppm; CDCl₃ + DMSO-d₆): δ = 24.40 (2H, s, C⁶H), 15.91 (2H, s, C⁴H), 16.64 (2H, s, C⁵H), 5.02 (10H, s, CH₃(C²) + CH₂(N¹)), 3.94 (6H, s, CH₃(N¹)), -3.01 (2H, s, N¹H) ppm. Magnetic moment: μₚ = 2.92 BM.
[Ni(κ²-N³,S-HattscN-Me)₂] (16)

It was prepared by a method similar to that for complex 13. Color: brown (74 %, M.p. 215–216 °C). Anal. Calcd. for C₁₆H₂₀N₆NiS₄: C, 39.72; H, 4.13; N, 17.38 %. Found: C, 39.65; H, 4.15; N, 16.93 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N–H) 3395br; ν(C–H) 3056m, 2905m, 2828w; ν(C=N) + ν(C=C) 1558s, 1507s; ν(C–N) 1069s, 1025m, 978s; ν(C–S) 743s. Electronic absorption spectrum (10⁻⁴ M in CH₃OH, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 412 (0.40 × 10⁴), 337 (1.28 × 10⁴), 270 (1.10 × 10⁴), 229 (1.09 × 10⁴). ¹H NMR (δ, ppm; CDCl₃ + DMSO-d₆): δ = 7.45 (2H, t, C₆H), 6.91 (2H, s, N₁H), 6.57 (2H, s, C₄H), 6.22 (2H, s, C₅H), 3.81 (6H, s, CH₃(C²)), 1.56 (6H, s, CH₃(N¹) + DMSO) ppm.

[Ni(κ²-N³,S-HattscN-Et)₂] (17)

It was prepared by a method similar to that for complex 13. Color: brown (74 %, M.p. 210–212 °C). Anal. Calcd. for C₁₈H₂₄N₆NiS₄: C, 42.24; H, 4.69; N, 16.43 %. Found: C, 42.17; H, 5.00; N, 16.48%. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3357br; ν(C–H) 3093m, 3056m, 2987m, 2871m; ν(C=N) + ν(C=C) 1560s, 1507s; ν(C–N) 1074s, 1046m, 1002m; ν(C–S) 737s. Electronic absorption spectrum (10⁻⁴ M in CH₃OH, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 410 (0.40 × 10⁴), 337 (1.28 × 10⁴), 270 (1.10 × 10⁴), 229 (1.09 × 10⁴). ¹H NMR (δ, ppm; CDCl₃ + DMSO-d₆): δ = 7.37 (2H, dd, C₆H), 6.71 (12H, d, C⁶H), 6.47 (2H, d, C⁵H), 6.10 (2H, s, N¹H), 4.24 (4H, s, CH₂), 2.20 (6H, s, CH₃(C²)) + DMSO, 1.56 (6H, s, CH₃(N¹)) ppm.

[Ni(κ²-N³,S-HattscN-Ph)₂] (18)

It was prepared by a method similar to that for complex 13. Color: black (68 %, M. p. 155 – 160 °C). Anal. Calcd. for C₂₆H₂₄N₆NiS₄: C, 51.43; H, 3.96; N, 13.84 %. Found: C, 50.92; H, 3.84; N, 13.32 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3408br; ν(C–H) 3098m,
2980m; ν(C=N) + ν(C=C) 1558s, 1507s; ν(C–N) 1050s, 1025m; ν(C–S) 752s. Electronic absorption spectrum (10⁻⁴ M in CH₃OH, λ_max/nm, ε /L mol⁻¹ cm⁻¹): 415 (0.52 × 10⁴), 343 (1.89 × 10⁴), 264 (2.28 × 10⁴), 213 (1.50 × 10⁴). ¹H NMR (δ, ppm; CDCl₃): δ = 8.88 (2H, d, N¹H) 7.46 (4H, m, o-Hₕₗ), 7.37 (2H, d, C⁶H), 7.30 (2H, m, p-Hₕₗ) + CDCl₃), 7.14 (2H, t, C⁴H), 7.04 (4H, m, m-Hₕₗ), 6.92 (2H, q, C⁵H), 2.80 (6H, s, CH₃(C²)) ppm.

[Ni(κ³-O,N³,S-stscN-Me)(κ¹-N-py)] (19)

To a solution of H₂stscN-Me (0.021 g, 0.100 mmol) in methanol was added solid Ni(OAc)₂ salt (0.025 g, 0.100 mmol) and stirred. The rust colored precipitates formed during stirring were filtered and allowed to dry at room temperature. The analytical data supported the formation of compound of empirical composition, {Ni(stscN-Me)} {Anal. Calcd for C₉H₉NiN₃OS:  C, 40.65; H, 3.39; N, 15.81 %. Found: C, 40.84; H, 3.23; N, 15.75 %}. To a suspension of {Ni(stscN-Me)} (0.025 g, 0.094 mmol) in acetonitrile was added pyridine (0.5 cm³), and contents were stirred for 1 h. The clear solution obtained was allowed to evaporate at room temperature which yielded red colored crystals. Color: red (69%, M.p. 192–194 °C). Anal. Calcd. for C₁₄H₁₄NiN₄OS:  C, 48.69; H, 4.06; N, 16.23 %. Found: C, 48.52; H, 4.21; N, 16.15 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3421br; ν(C–H) 3084w, 3020w, 2988w, 2887; ν(C=O) + ν(C=C) 1603s, 1524s; ν(C–N) 1070s, 1022s, 943s; ν(C–S) 771s. Electronic absorption spectrum (10⁻⁴ M in CH₃OH, λ_max/nm, ε /L mol⁻¹ cm⁻¹): 405 (1.36 × 10⁴), 366 (1.73 × 10⁴), 318 (2.35 × 10⁴), 307 (2.40 × 10⁴), 266 (2.50 × 10⁴). ¹H NMR (δ, ppm; CDCl₃): δ = 8.88 (1H, s, o-Hₕ), 7.88 (1H, s, C₂H), 7.44 (1H, t, p-Hₕ), 7.31 (2H, t, m-Hₕ), 7.18 (2H, m, C⁵H + C⁶H), 6.85 (1H, d, C⁸H), 6.63 (1H, t, C⁷H), 4.61 (1H, d, N¹H), 2.90 (3H, d, CH₃) ppm.

[Ni(κ³-O,N³,S-stscN-Ph)(κ¹-N-py)] (20)

It was prepared by a method similar to that for complex 19. Color: red (71%, M.p. above 300 °C). Anal. Calcd. for C₂₆H₂₂N₈Si₂:  C, 54.81; H, 3.86; N, 19.67 %. Found: C, 54.65; H, 4.08; N, 19.51 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3424br; ν(C–H) 3053w, 3014w, 2956m; ν(C=O) +
v(C=C) 1602s, 1544s; v(C–N), 1091s, 1022s, v(C–S) 769s. Electronic absorption spectrum (10^{-4} M in CH_3OH, \lambda_{max}/nm, \varepsilon/L \text{mol}^{-1} \text{cm}^{-1}): 414 (0.86 \times 10^{4}), 370 (1.23 \times 10^{4}), 320 (1.35 \times 10^{4}), 260 (2.13 \times 10^{4}), 229 (2.23 \times 10^{4}). ^1H NMR (\delta, ppm; CDCl_3): \delta = 8.84 (2H, sb, o-Hpy), 8.06 (1H, s, C^2H), 7.77 (1H, t, p-Hpy), 7.47 (2H, d, o-Hph), 7.24 (6H, m, N^1H+m-Hpy+p-m-Hph), 6.99 (2H, t, C^5H + C^6H), 6.88(1H, d, C^8H), 6.65 (1H, t, C^7H) ppm.

[\text{Ni}(\kappa^2-O,N^3,S-stscN-Me)(\kappa^1-P-PPh_3)] (21)

To a light green solution of NiCl_2 salt (0.116 g, 0.116 mmol) in acetonitrile was added solid H_2stscN-Me (0.024 g, 0.116 mmol) followed by the addition of Et_3N base (1mL) and stirred for 1h. To this was added PPh_3 (0.030 g, 0.116 mmol) and stirred the contents for about 4h. The clear red solution was allowed to evaporate at room temperature which yielded red colored crystals along with the formation of Et_3NH^+Cl^- salt. Color: red (57%, M.p. 180–182 °C). Anal. Calcd. for C_{27}H_{24}NiN_3OPS:  C, 61.34; H, 4.54; N, 7.95 %. Found: C, 61.56 ; H, 4.39; N, 7.89 %.

IR (KBr, cm^{-1}, selected absorption bands): v(N^1–H) 3428br; v(C–H) 3070w, 3047w, 2887w, 2865w; v(C=N) + v(C=C) 1607s, 1528s; v(P–C_{ph}) 1097s; v(C–N) 1024s, 1001s, 916s; v(C–S) 778s. Electronic absorption spectrum (10^{-4} M in DMSO, \lambda_{max}/nm, \varepsilon/L \text{mol}^{-1} \text{cm}^{-1}): 409 (0.46 \times 10^{4}), 363 (0.78 \times 10^{4}), 301 (1.25 \times 10^{4}), 232 (2.26 \times 10^{4}). ^1H NMR (\delta, ppm; CDCl_3): \delta = 8.34 (1H, d, C^2H), 7.79 (6H, m, o-Hph), 7.46 (9H, m, p-m-Hph), 7.24 (1H, dd, C^2H), 7.06 (1H, t, C^6H), 6.59 (1H, t, C^8H), 6.41 (1H, d, C^7H), 4.74 (1H, db, N^1H), 2.90 (3H, d, CH_3) ppm. ^31P NMR (\delta, ppm; CDCl_3): \delta = 20.41 ppm; \Delta \delta(\delta_{\text{complex}}–\delta_{\text{PPh_3}}) = 25.11 ppm.

[\text{Ni}(\kappa^2-O,N^3,S-stscN-Et)(\kappa^1-P-PPh_3)] (22)

It was prepared by a method similar to that for complex 21. Color: red-violet (53%, M.p. 198–200 °C). Anal. Calcd. for C_{28}H_{26}NiN_3OPS:  C, 61.85; H, 4.97; N, 7.73 %. Found: C, 62.12; H, 4.67; N, 7.95 %. IR (KBr, cm^{-1}, selected absorption bands): v(N^1–H) 3420br; v(C–H) 3078w, 3055w, 2976w, 2929w, 2878m; v(C=N) + v(C=C) 1600s, 1541s; v(P–C_{ph}) 1097s; v(C–N), 1045m, 1026m, 920m; v(C–S) 787s. Electronic absorption spectrum (10^{-4} M in CH_3OH, \lambda_{max}/nm, \varepsilon/L \text{mol}^{-1} \text{cm}^{-1}): 409 (0.47 \times 10^{4}), 364 (0.78 \times 10^{4}), 302 (1.25 \times 10^{4}), 232 (2.26 \times
$H N M R (\delta, ppm; CDCl_3): \delta = 8.32 (1H, d, C^2H), 7.80 (6H, m, o-H_{Ph}), 7.44 (9H, m, p- + m-H_{Ph}), 7.26 (1H, d, C^5H), 7.07 (1H, t, C^6H), 6.60 (1H, t, C^8H), 6.41 (1H, d, C^7H), 4.71 (1H, sb, N^1H), 3.31 (2H, m, CH_2), 1.13 (3H, t, CH_3) ppm. $3^1P N M R (\delta, ppm; CDCl_3): \delta = 20.56 ppm; \Delta \delta(\delta_{\text{complex}}-\delta_{\text{PPh}_3}) = 25.29 ppm.

$[\text{Ni}(\kappa^2-O,N^2,S-stscN-Ph)(\kappa^1-N-2-Phpy)] (23)$

It was prepared by a method similar to that for complex 19. Color: brown-red (72%, M.p. 175–177 °C). Anal. Calcd. for C$_{25}$H$_{20}$NiN$_4$S: C, 61.92; H, 4.11; N, 12.10 %. Found: C, 61.92; H, 4.11; N, 12.10 %. IR (KBr, cm$^{-1}$, selected absorption bands): $\nu$(N$^1$–H) 3436br; $\nu$(C–H) 3105w, 3080w, 2986w; $\nu$(C=N) + $\nu$(C=C) 1598s, 1517s; $\nu$(C–N) 1075s, 1019s, 942w; $\nu$(C–S) 763s. Electronic absorption spectrum (0.5×10$^{-4}$ M in DMSO, $\lambda_{\text{max}}$/nm, $\epsilon$/L mol$^{-1}$ cm$^{-1}$): 428 (0.84 × 10$^4$), 378 (1.31 × 10$^5$), 317 (1.36 × 10$^5$), 296 (1.99 × 10$^4$), 287 (2.81 × 10$^4$). $^1H N M R (\delta, ppm; CDCl_3): \delta = 9.56 (1H, s, C^2H), 8.65 (2H, dd, C^9H + C^5H), 8.62 (1H, d, C^{12}H), 8.00–7.15 (10H, m, o-H + p-H + m-H), 7.14 (1H, m, N^1H), 7.08 (2H, m, C^{10}H + C^{11}H), 6.71 (3H, m, C^8H + C^6H + C^7H) ppm.

$[\text{Ni}(stsc)_2(bipy)(OH_2)] (24)$

Reaction of Ni(OAc)$_2$ (0.025 g, 0.100 mmol) with the salicyladehyde thiosemicarbazone (H$_2$stsc) (0.020 g, 0.100 mmol) in methanol in 1 : 1 molar ratio formed a solid with composition {Ni(stsc)}. To the suspension of {Ni(stsc)} (0.025 g, 0.100 mmol) in acetonitrile (10 mL) was added solid bipyridine (0.008 g, 0.050 mmol). The contents were stirred and after a few minutes a clear red solution was formed. During stirring period of 4 h, red compound started forming, which was filtered and dried. Crystals for X-ray were grown in dichloromethane, acetonitrile and methanol mixture (1:1:1 :: v/v). Color: red-brown (74%, M.p. dec. at 275 °C). Anal. Calcd. for C$_{26}$H$_{24}$Ni$_3$N$_2$O$_3$ S$_2$: C, 46.01; H, 3.54; N, 16.52 %. Found: C, 45.52; H, 3.59; N, 16.85 %. IR (KBr, cm$^{-1}$, selected absorption bands): $\nu$(N$^1$–H) 3412br; $\nu$(O–H) 3158s; $\nu$(C–H) 3376s; $\nu$(C–S) 763s. Electronic absorption spectrum (0.5×10$^{-4}$ M in DMSO, $\lambda_{\text{max}}$/nm, $\epsilon$/L mol$^{-1}$ cm$^{-1}$): 428 (0.84 × 10$^4$), 378 (1.31 × 10$^5$), 317 (1.36 × 10$^5$), 296 (1.99 × 10$^4$), 287 (2.81 × 10$^4$). $^1H N M R (\delta, ppm; CDCl_3): \delta = 8.32 (1H, d, C^2H), 7.80 (6H, m, o-H_{Ph}), 7.44 (9H, m, p- + m-H_{Ph}), 7.26 (1H, d, C^5H), 7.07 (1H, t, C^6H), 6.60 (1H, t, C^8H), 6.41 (1H, d, C^7H), 4.71 (1H, sb, N^1H), 3.31 (2H, m, CH_2), 1.13 (3H, t, CH_3) ppm. $3^1P N M R (\delta, ppm; CDCl_3): \delta = 20.56 ppm; \Delta \delta(\delta_{\text{complex}}-\delta_{\text{PPh}_3}) = 25.29 ppm.
3018s, 2918w, 2895w; ν(C=N) + ν(C=C) 1601s, 1520s; ν(C–N) 1018s, 928s; ν(C–S) 771s.

Electronic absorption spectrum (0.5×10⁻⁴ M in DMSO, Λₘₐₓ/nm, ε/L mol⁻¹ cm⁻¹): 421 (1.07 × 10⁴), 375 (2.82 × 10⁴), 305 (2.48 × 10⁴), 291 (3.11 × 10⁴), 274 (4.05 × 10⁴), 267 (4.88 × 10⁴), 260 (4.90 × 10⁴). Magnetic moment: μₑᶠᶠ = 2.97 BM.

**[Ni₂(stscN-Me)₂(bipy)(OHMe)]·2.56(MeOH)·0.44(H₂O)** (25)

It was prepared by a method similar to that for complex 24. Color: red (70 %, M.p. dec. at 282 °C). Anal. Calcd. for C₃₁.₅₆H₄₁.₁₃N₈Ni₂O₆S₂: C, 46.75; H, 5.08; N, 13.82 %. Found: C, 46.79; H, 5.12; N, 13.78 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3434br; ν(O–H) 3398s; ν(C–H) 3063s, 2903w, 2831w; (C=N) + (C=C) 1585s, 1508s; (C–N) 1022s, 914s; (C–S) 763s.

Electronic absorption spectrum (0.5×10⁻⁴ M in DMSO, Λₘₐₓ/nm, ε/L mol⁻¹ cm⁻¹): 420 (0.88 × 10⁴), 374 (1.77 × 10⁴), 352 (2.53 × 10⁴), 338 (2.62 × 10⁴), 305 (2.61 × 10⁴), 293 (2.59 × 10⁴), 268 (3.02 × 10⁴), 263 (3.30 × 10⁴). Fluorescence spectrum: Λₘₐₓₑₓ = 337 nm, Λₘₐₓₑₘ = 384, 480 nm. Magnetic moment: μₑᶠᶠ = 3.29 BM.

**[Ni₂(stscN-Et)₂(bipy)]** (26a)

It was prepared by a method similar to that for complex 24. Crystals for X-ray were grown in acetonitrile. Color: red (71 %, M. p. 262 – 264 °C). Anal. Calcd. for C₃₀H₃₀N₈Ni₂O₂S₂: C, 50.27; H, 4.19; N, 15.64 %. Found: C, 50.23; H, 4.22; N, 15.67 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3391br; ν(O–H) 3398s; ν(C–H) 3063s, 2903w, 2831w; ν(C=N) + ν(C=C) 1585s, 1508s; ν(C–N) 1022s, 914s; ν(C–S) 763s.

Electronic absorption spectrum (0.5×10⁻⁴ M in DMSO, Λₘₐₓ/nm, ε/L mol⁻¹ cm⁻¹): 422 (1.02 × 10⁴), 373 (2.02 × 10⁴), 310 (1.99 × 10⁴), 294 (2.59 × 10⁴), 284 (3.04 × 10⁴), 275 (3.59 × 10⁴), 272 (3.65 × 10⁴). Fluorescence spectrum: Λₘₐₓₑₓ = 337 nm, Λₘₐₓₑₘ = 398 nm. Magnetic moment: μₑᶠᶠ = 3.28 BM.

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It was prepared by the crystallization of complex 26a in a mixture of dichloromethane, acetonitrile and methanol.

It was prepared by a method similar to that for complex 24. Color: red (71 %, M.p. 195–197 °C) Anal. Calcd. for C_{38}H_{30}N_{8}Ni_{2}O_{2}S_{2}: C, 56.20; H, 3.70; N, 13.80 %. Found: C, 56.97; H, 3.86; N, 14.14 %. IR (KBr, cm\(^{-1}\), selected absorption bands): \(\nu\)(N–H) 3397br; \(\nu\)(C–H) 3020m, 2994w; \(\nu\)(C=N) + \(\nu\)(C=C) 1597s, 1544s; \(\nu\)(C–N) 1016s, 928s; \(\nu\)(C–S) 756s. Electronic absorption spectrum (0.5 \times 10^{-4} M in DMSO, \(\lambda_{\text{max}}/nm, \epsilon/L\ \text{mol}^{-1}\ \text{cm}^{-1}\)): 426 (0.75 \times 10^{4}), 380 (1.20 \times 10^{4}), 324 (1.27 \times 10^{4}), 308 (1.62 \times 10^{4}), 281 (3.42 \times 10^{4}), 274 (3.33 \times 10^{4}). Fluorescence spectrum: \(\lambda_{\text{max}}^{\text{ex}} = 337\ \text{nm}, \lambda_{\text{max}}^{\text{em}} = 416\ \text{nm}.

Magnetic moment: \(\mu_{\text{eff}} = 3.12\ \text{BM}.

To a suspension of \{Ni(5-Me-hbtscN-Me)\} (0.020 g, 0.071 mmol) in acetonitrile (10 mL) was added solid bipyridine (0.006 g, 0.035 mmol) and stirred. During stirring, solution became clear. This solution was allowed to evaporate at room temperature, which led to the formation of sticky mass. This mass was crystallized in methanol and dichloromethane mixture (3:1 :: v/v). Color: red-orange (70 %, M.p. above 300 °C). Anal. Calcd. for C_{33}H_{42}N_{8}Ni_{2}O_{5}S_{2}: C, 48.75; H, 5.17; N, 13.79
%. Found: C, 48.72; H, 5.13; N, 13.82 %. IR (KBr, cm^{-1}, selected absorption bands): \( \nu(N^1-H) \) 3412br; \( \nu(O-H) \) 3378s; \( \nu(C-H) \) 3018s, 2930w, 2845m; \( \nu(C=N) + \nu(C=C) \) 1595s, 1545s; \( \nu(C-N) \) 1027s, 938s; \( \nu(C-S) \) 758s.

Electronic absorption spectrum (0.5 \times 10^{-4} M in DMSO, \( \lambda_{\text{max}}/\text{nm}, \varepsilon/L \text{ mol}^{-1} \text{ cm}^{-1} \)): 424 (0.95 \times 10^{4}), 373 (1.94 \times 10^{4}), 310 (1.84 \times 10^{4}), 294 (2.38 \times 10^{4}), 273 (3.47 \times 10^{4}), 270 (3.62 \times 10^{4}), 261 (4.17 \times 10^{4}). Magnetic moment: \( \mu_{\text{eff}} = 3.28 \text{ BM} \).

[\text{Ni}_2(5-\text{Me-hbtscN-Et})_2(bipy)(\text{OHMe})]\cdot\text{MeOH} (29)

It was prepared by a method similar to that for complex 28. Crystals for X-ray were grown in dichloromethane and methanol mixture (3:1 :: v/v). Color: red-orange (70 %, M.p. 210–212 °C). Anal. Calcd. for \( \text{C}_{33}\text{H}_{42}\text{N}_8\text{Ni}_2\text{O}_4\text{S}_2 \): C, 49.79; H, 5.28; N, 14.08 %. Found: C, 50.12; H, 5.23; N, 13.98 %.

Electronic absorption spectrum (0.5 \times 10^{-4} M in DMSO, \( \lambda_{\text{max}}/\text{nm}, \varepsilon/L \text{ mol}^{-1} \text{ cm}^{-1} \)): 428 (1.30 \times 10^{4}), 375 (2.42 \times 10^{4}), 313 (2.38 \times 10^{4}), 303 (2.7 \times 10^{4}), 294 (3.14 \times 10^{4}), 284 (3.84 \times 10^{4}), 278 (4.07 \times 10^{4}). Magnetic moment: \( \mu_{\text{eff}} = 3.01 \text{ BM} \).

[\text{Ni}_2(5-\text{NO}_2-\text{hbtscN-Me})_2(bipy)_2]\cdot0.5\text{H}_2\text{O} (30)

To a suspension of \{\text{Ni}(5-\text{NO}_2-\text{hbtscN-Me})\} (0.020 g, 0.064 mmol) in acetonitrile was added solid bipyridine (0.010 g, 0.064 mmol). The contents were stirred till a clear solution was obtained. The solution was refluxed for 15 min. After cooling kept it for crystallization at room temperature, from which red crystals get separated over a period of 2 days. Color: red (70 %, M. p. above 300 °C). Anal. Calcd. for \( \text{C}_{38}\text{H}_{33}\text{N}_{12}\text{Ni}_2\text{O}_{6.50}\text{S}_2 \): C, 48.34; H, 3.50; N, 17.81 %. Found: C, 48.72; H, 3.67; N, 17.58 %.

IR (KBr, cm^{-1}, selected absorption bands): \( \nu(N^1-H) \) 3345br; \( \nu(C-H) \) 3007s, 2935w, 2845w; \( \nu(C=N) + \nu(C=C) \) 1578s, 1545s; \( \nu(C-N) \) 1027s, 915s; \( \nu(C-S) \) 765s. Electronic absorption spectrum (0.5 \times 10^{-4} M in DMSO, \( \lambda_{\text{max}}/\text{nm}, \varepsilon/L \text{ mol}^{-1} \text{ cm}^{-1} \)):...
430 (2.97 \times 10^4), 401 (3.82 \times 10^4), 393 (3.78 \times 10^4), 386 (3.78 \times 10^4), 376 (3.82 \times 10^4), 362 (3.81 \times 10^4), 355 (2.33 \times 10^4), 340 (2.80 \times 10^4), 303 (3.91 \times 10^4), 294 (3.92 \times 10^4), 285 (3.35 \times 10^4), 260 (3.14 \times 10^4). Magnetic moment: \( \mu_{\text{eff}} = 3.38 \) BM.

\[ \text{[Ni(\kappa^3-O,N^3,S-5-NO}_2\text{-hhtseN-Et)(\kappa^2-N,N-bipy)] (3J)} \]

It was prepared by a method similar to that for complex 30. Color: red-brown (69 \%, M.p. 228–230 °C). Anal. Calcd. for C_{20}H_{18}N_{6}NiO_{3}S: C, 49.88; H, 3.74; N, 17.46 \%. Found: C, 50.02; H, 3.61; N, 17.78 \%. IR (KBr, cm\(^{-1}\), selected absorption bands): \( \nu(\text{N}^1-\text{H}) \) 3345br; \( \nu(\text{C}–\text{H}) \) 3056s, 2925w, 2867w; \( \nu(\text{C}=\text{N}) + \nu(\text{C}–\text{C}) \) 1597s, 1469s; \( \nu(\text{C}–\text{N}) \) 952s; \( \nu(\text{C}–\text{S}) \) 758s. Electronic absorption spectrum (0.5 \times 10^{-4} M in DMSO, \( \lambda_{\text{max}}/\text{nm}, \varepsilon/L \text{ mol}^{-1} \text{ cm}^{-1} \)): 428 (0.30 \times 10^4), 398 (0.36 \times 10^4), 367 (0.38 \times 10^4), 304 (0.46 \times 10^4), 282 (0.81 \times 10^4), 275 (0.76 \times 10^4), 260 (0.68 \times 10^4). Magnetic moment: \( \mu_{\text{eff}} = 2.98 \) BM.

\[ \text{[Ni(\kappa^3-O,N^3,S-hacptscN-Me)(\kappa^2-N,N-bipy)(\kappa^1-O-OHMe)] (32)} \]

To a suspension of \{Ni(hacptscN-Me)\} (0.010 g, 0.036 mmol) in acetonitrile was added solid bipyridine (0.006 g, 0.036 mmol) and stirred for 2 h. During stirring, the color of the solution changed from brown to red. The filtered solution was allowed to evaporate at room temperature which led to the formation of sticky mass. This mass was crystallized in dichloromethane and methanol mixture (3:1 :: v/v). Color: red-brown (67 \%, M.p. 210–212 °C). Anal. Calcd. for C_{21}H_{23}N_{5}NiO_{2}S: C, 53.88; H, 4.92; N, 14.97 \%. Found: C, 54.12; H, 4.83; N, 15.01 \%. IR (KBr, cm\(^{-1}\), selected absorption bands): \( \nu(\text{N}^1–\text{H}) \) 3430br; \( \nu(\text{O}–\text{H}) \) 3382s; \( \nu(\text{C}–\text{H}) \) 3072w, 2925m, 2858w; \( \nu(\text{C}=\text{N}) + \nu(\text{C}–\text{C}) \) 1597s, 1562s; \( \nu(\text{C}–\text{N}) \) 1061m, 1019m; \( \nu(\text{C}–\text{S}) \) 764s. Electronic absorption spectrum (0.5 \times 10^{-4} M in DMSO, \( \lambda_{\text{max}}/\text{nm}, \varepsilon/L \text{ mol}^{-1} \text{ cm}^{-1} \)): 416 (0.24 \times 10^4), 370 (0.50 \times 10^4), 307 (0.90 \times 10^4), 293 (1.12 \times 10^4), 285 (1.18 \times 10^4), 266 (1.54 \times 10^4). Magnetic moment: \( \mu_{\text{eff}} = 2.98 \) BM.
[Ni(κ^3-O,N^3, S-hacptsc-Et)(κ^3-N,N-bipy)(κ^1-O-OH_2)] (33)

To a suspension of {Ni(hacptsc-Et)} (0.020 g, 0.067 mmol) in acetonitrile was added solid bipyridine (0.010 g, 0.067 mmol) and stirred for 2 h. During stirring, the color of the solution changes from brown to reddish brown and the filtered solution was kept for crystallization. Color: red-brown (65 %, M.p. 180–182 °C). Anal. Calcd. for C_{21}H_{23}N_{5}NiO_{2}S: C, 53.82; H, 4.91; N, 14.95 %. Found: C, 54.06; H, 4.69; N, 14.73 %. IR (KBr, cm\(^{-1}\), selected absorption bands): \(\nu(\text{N–H})\) 3404 \text{br}; \(\nu(\text{O–H})\) 3367 \text{s}; \(\nu(\text{C–H})\) 3042 \text{s}, 2952 \text{w}, 2922 \text{w}, 2867 \text{m}; \(\nu(\text{C=N})\) + \(\nu(\text{C–C})\) 1565 \text{s}, 1535 \text{s}; \(\nu(\text{C–N})\) 1057 \text{s}, 1020 \text{m}, 937 \text{s}; \(\nu(\text{C–S})\) 761 \text{s}.

Electronic absorption spectrum (0.5 × 10\(^{-4}\) M in DMSO, \(\lambda_{\text{max}}\)/nm, \(\varepsilon/L\text{ mol}^{-1}\text{ cm}^{-1}\)): 419 (0.31 × 10\(^4\)), 373 (0.61 × 10\(^4\)), 308 (0.76 × 10\(^4\)), 294 (0.80 × 10\(^4\)), 268 (1.26 × 10\(^4\)), 262 (1.36 × 10\(^4\)). Magnetic moment: \(\mu_{\text{eff}}\) = 3.05 BM.

[\text{Ni}_2(\kappa^3-\text{O}, \kappa^3\text{-S-stsc-Me})_2(\mu-\text{N,N-4,4’-bipy}) (34)

To a suspension of \{\text{Ni(stsc-Me)}\} (0.025 g, 0.090 mmol) in acetonitrile was added solid 4,4’-bipyridine (0.007 g, 0.045 mmol). The contents were stirred and after a few minutes a clear red solution was formed. During stirring period of 4 h, red compound started forming, which was filtered and dried. Color: red (65 %, M.p. 270 °C(dec)). Anal. Calcd. for C_{28}H_{26}N_{8}Ni_{2}O_{2}S_{2}: C, 48.21; H, 4.15; N, 15.93 %. Found: C, 48.87; H, 3.78; N, 16.29 %. IR (KBr, cm\(^{-1}\), selected absorption bands): \(\nu(\text{N–H})\) 3411 \text{br}; \(\nu(\text{O–H})\) 3042 \text{s}, 2952 \text{w}, 2922 \text{w}, 2867 \text{m}; \(\nu(\text{C=N})\) + \(\nu(\text{C–C})\) 1544 \text{s}, 1468 \text{s}; \(\nu(\text{C–N})\) 1057 \text{s}, 1020 \text{m}, 937 \text{s}; \(\nu(\text{C–S})\) 754 \text{s}.

Electronic absorption spectrum (10\(^{-4}\) M in DMSO, \(\lambda_{\text{max}}\)/nm, \(\varepsilon/L\text{ mol}^{-1}\text{ cm}^{-1}\)): 422 (0.61 × 10\(^4\)), 374 (1.28 × 10\(^4\)), 353 (1.74 × 10\(^4\)), 338 (1.73 × 10\(^4\)), 307 (1.89 × 10\(^4\)), 297 (3.61 × 10\(^4\)), 270 (4.31 × 10\(^4\)), 267 (4.41 × 10\(^4\)).
[Ni<sub>2</sub>(κ<sup>3</sup>-O,N<sup>3</sup>,S-stsc-N-Et)<sub>2</sub>(μ-N,N-4,4′-bipy)] (35)

It was prepared by a method similar to that for complex 34. Color: red (69 %, M.p. 250–252 °C). Anal. Calcd. for C<sub>30</sub>H<sub>26</sub>N<sub>8</sub>Ni<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 50.60; H, 3.65; N, 15.74 %. Found: C, 50.28; H, 4.26; N, 15.76 %. IR (KBr, cm<sup>-1</sup>, selected absorption bands): ν(N<sup>1</sup>–H) 3434br; ν(C–H) 2997m, 2924w, 2854m; ν(C=N) + ν(C=C) 1560s, 1472s; ν(C=N) 1072s, 1042m, 903s; ν(C–S) 775s. Electronic absorption spectrum (10<sup>-4</sup> M in DMSO, λ<sub>max</sub>/nm, ε/L mol<sup>-1</sup> cm<sup>-1</sup>): 421 (1.02 × 10<sup>4</sup>), 375 (1.95 × 10<sup>4</sup>), 359 (1.74 × 10<sup>4</sup>), 313 (1.89 × 10<sup>4</sup>), 306 (1.04 × 10<sup>4</sup>), 281 (2.29 × 10<sup>4</sup>), 276 (2.55 × 10<sup>4</sup>).

[Ni<sub>2</sub>(κ<sup>3</sup>-O,N<sup>3</sup>,S-hacptsc-N-Me)<sub>2</sub>(μ-N,N-4,4′-bipy)] (36)

It was prepared by a method similar to that for complex 34. Color: red-brown (69 %, M.p. 272–274 °C). Anal. Calcd. for C<sub>30</sub>H<sub>30</sub>N<sub>8</sub>Ni<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 50.56; H, 4.21; N, 15.73 %. Found: C, 51.14; H, 4.69; N, 15.82 %. IR (KBr, cm<sup>-1</sup>, selected absorption bands): ν(N<sup>1</sup>–H) 3427br; ν(C–H) 3011m, 2923w, 2868w; ν(C=N) + ν(C=C) 1599s, 1530s; ν(C=N) 1027s, 931s; ν(C–S) 771s. <sup>1</sup>H NMR (δ, ppm; CDCl<sub>3</sub>): δ = 8.96–7.51 (8H, m, H<sub>4,4′</sub>-bipy), 7.23 (2H, d, C<sup>5</sup>H + CDCl<sub>3</sub>), 7.05 (2H, t, C<sup>6</sup>H), 6.85 (2H, d, C<sup>8</sup>H), 6.66 (2H, t, C<sup>7</sup>H), 4.54 (2H, sb, N<sup>1</sup>H), 2.92 (6H, d, CH<sub>3</sub>(C<sup>2</sup>)), 2.68 (6H, s, CH<sub>3</sub>(N<sup>1</sup>)) ppm. Electronic absorption spectrum (0.5 × 10<sup>-4</sup> M in DMSO, λ<sub>max</sub>/nm, ε/L mol<sup>-1</sup> cm<sup>-1</sup>): 419 (0.91 × 10<sup>4</sup>), 371 (1.79 × 10<sup>4</sup>), 307 (2.08 × 10<sup>4</sup>), 296 (1.84 × 10<sup>4</sup>), 269 (3.46 × 10<sup>4</sup>), 266 (3.71 × 10<sup>4</sup>).
[Ni₂(κ³-O,N³,S-hacptscN-Et)₂(μ-N,N-4,4'-bipy)] (37)

It was prepared by a method similar to that for complex 34. Color: red-brown (66 %, M.p. 280–282 °C). Anal. Calcd. for C₃₂H₃₄N₈Ni₂O₂S: C, 51.59; H, 4.57; N, 15.05 %. Found: C, 51.14; H, 4.69; N, 14.82 %. IR (KBr, cm⁻¹, selected absorption bands): v(N¹-H) 3405br; v(C–H) 3009m, 2962m, 2924m, 2858w; v(C=N) + v(C–C) 1597s, 1536s; v(C–N) 1025s, 911s; v(C–S) 758s. ¹H NMR (δ, ppm; CDCl₃): δ = 8.98–7.50 (8H, m, H₄,₄'-bipy), 7.28 (2H, d, C₅H + CDCl₃), 7.15 (2H, s, C₈H), 6.84 (2H, s, C₆H), 6.30 (2H, s, C₇H), 4.30 (2H, s, C₁H), 3.35 (4H, d, CH₂), 2.67 (6H, s, CH₃(C²)), 1.21 (6H, s, CH₃(N¹)) ppm. Electronic absorption spectrum (10⁻⁴ M in DMSO, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 416 (0.93 × 10⁴), 368 (1.71 × 10⁴), 316 (1.72 × 10⁴), 309 (1.85 × 10⁴), 304 (1.80 × 10⁴), 298 (1.76 × 10⁴), 279 (2.29 × 10⁴).

[M₂(stscN-Et)₂(dmbipy)(OH₂)]·2H₂O (38)

It was prepared by a method similar to that for complex 24. Crystals for X-ray were grown in dichloromethane, acetonitrile and methanol mixture (1:1:1 :: v/v). Color: red (68 %, M.p. 250–252 °C). Anal. Calcd. for C₃₂H₄₀N₈Ni₂O₅S₂: C, 48.10; H, 5.01; N, 14.03 %. Found: C, 47.86; H, 4.91; N, 14.26 %. IR (KBr, cm⁻¹, selected absorption bands): v(N(H) 3412br; v(O–H) 3348s; v(C–H) 3020m, 2960w, 2875w; v(C=N) + v(C=C) 1582s, 1534s; v(C–N) 1028s, 930s; v(C–S) 767s. Electronic absorption spectrum (0.5 × 10⁻⁴ M in DMSO, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 420 (1.13 × 10⁴), 373 (2.12 × 10⁴), 307 (2.28 × 10⁴), 293 (2.99 × 10⁴), 276 (3.80 × 10⁴). Magnetic moment: µ_eff = 3.14 BM.
[Ni$_2$(stsc)$_2$(phen)(OH$_2$)] $\text{(39)}$

To the suspension of \{Ni(stsc)\} (0.025 g, 0.100 mmol) in acetonitrile (10 mL) was added solid phenanthroline (0.009 g, 0.050 mmol). The contents were stirred and after a few minutes a clear red solution was formed. During stirring period of 4 h, red compound started forming, which was filtered and dried. Color: red (65%, M.p. 265–267 °C). Anal. Calcd. for C$_{28}$H$_{24}$N$_8$Ni$_2$O$_3$S$_2$: C, 46.01; H, 3.54; N, 16.52 %. Found: C, 45.52; H, 3.59; N, 16.85 %.

IR (KBr, cm$^{-1}$, selected absorption bands): $\nu$(N–H) 3410br; $\nu$(O–H) 3365s; $\nu$(C–H) 3034s, 2937w, 2867m; $\nu$(C=N) + $\nu$(C=C) 1597s, 1534s; $\nu$(C–N) 1047s, 950s; $\nu$(C–S) 756s. Electronic absorption spectrum (0.5 × 10$^{-4}$ M in DMSO, $\lambda_{\text{max}}$/nm, $\varepsilon$/L mol$^{-1}$ cm$^{-1}$): 411 (1.22 × 10$^4$), 386 (1.24 × 10$^4$), 338 (1.03 × 10$^4$), 269 (5.32 × 10$^4$), 263 (4.22 × 10$^4$). Fluorescence spectrum: $\lambda_{\text{max}}^{\text{ex}}$ = 340 nm, $\lambda_{\text{max}}^{\text{em}}$ = 418, 488 nm. Magnetic moment: $\mu_{\text{eff}}$ = 3.12 BM.

[Co$_2$(bipy)$_2$(phen)$_2$(OH)$_2$] $\cdot$ CH$_3$COOH $\text{(40)}$

To a solution of H$_2$stscN-Me (0.008 g, 0.040 mmol) in acetonitrile (8 mL) was added solid Ni(OAc)$_2$ (0.010g, 0.040 mmol) and stirred. During stirring period of 1 h, rust colored precipitates started forming. To these precipitates was added solid phenanthroline (0.004 g, 0.020 mmol) and stirred the contents till clear red solution was obtained. This red solution was kept for slow evaporation. Sticky mass obtained after the evaporation of the solvent, was dissolved in methanol and dichloromethane mixture (3:1 :: v/v), from which red air stable crystals were obtained. Color: red (67%, M.p. 224–226 °C). Anal. Calcd. for C$_{32}$H$_{32}$N$_8$Ni$_2$O$_5$ S$_2$: C, 48.59; H, 4.05; N, 14.17 %. Found: C, 48.32; H, 3.89; N, 13.99 %. IR (KBr, cm$^{-1}$, selected absorption bands): $\nu$(N–H) 3402br; $\nu$(O–H) 3372s; $\nu$(C–H) 3053s, 2922w, 2878m; $\nu$(C=N) + $\nu$(C=C) 1593s, 1533s; $\nu$(C–N) 1018s, 908s; $\nu$(C–S) 752s. Electronic absorption spectrum (0.5 × 10$^{-4}$ M in DMSO, $\lambda_{\text{max}}$/nm, $\varepsilon$/L mol$^{-1}$ cm$^{-1}$): 415 (1.19 × 10$^4$), 380 (1.40 × 10$^4$), 337 (1.33 × 10$^4$), 294
(2.72 \times 10^4), 273 (5.57 \times 10^4), 265 (4.93 \times 10^4). Fluorescence spectrum: \( \lambda_{\text{max}}^{\text{ex}} = 340 \text{ nm}, \lambda_{\text{max}}^{\text{em}} = 388 \text{ nm} \). Magnetic moment: \( \mu_{\text{eff}} = 3.01 \text{ BM} \).

\[ \text{[Ni}\text{(_{2}stscN-Et)}\text{(_2phen)(OH}_{2}\text{)]\cdotH}_{2}\text{O (41)} \]

To a suspension of \{Ni(stscN-Et)\} (0.020 g, 0.071 mmol) in acetonitrile (8 mL) was added solid phenanthroline (0.007, 0.035 mmol) and stirred for 1h. The color of the solution changed from rust to dark purple. The filtered solution was kept for crystallization at room temperature. Crystals get separated after three days. Color: purple (67%, M.p. 240–242 °C) Anal. Calcd. for C_{32}H_{34}N_8Ni_2O_4S_2: C, 49.47; H, 4.38; N, 14.43 %. Found: C, 49.77; H, 4.89; N, 14.54 %. IR (KBr, cm^{-1}, selected absorption bands): \( \nu(\text{N–H}) 3412\text{br} \); \( \nu(\text{O–H}) 3389\text{s} \); \( \nu(\text{C–H}) 3020\text{m}, 2924\text{w}, 2867\text{m} \); \( \nu(\text{C=N}) + \nu(\text{C=C}) 1597\text{s}, 1545\text{s} \); \( \nu(\text{C–N}) 1029\text{s}, 916\text{s} \); \( \nu(\text{C–S}) 756\text{s} \).

Electronic absorption spectrum (0.5 \times 10^{-4} \text{ M in DMSO, } \lambda_{\text{max}}/\text{nm, } e/\text{L mol}^{-1} \text{ cm}^{-1}): 418 (1.03 \times 10^4), 383 (1.30 \times 10^4), 343 (1.21 \times 10^4), 320 (1.35 \times 10^4), 296 (2.34 \times 10^4), 274 (5.19 \times 10^4), 269 (4.83 \times 10^4). Fluorescence spectrum: \( \lambda_{\text{max}}^{\text{ex}} = 340 \text{ nm}, \lambda_{\text{max}}^{\text{em}} = 384 \text{ nm} \). Magnetic moment: \( \mu_{\text{eff}} = 3.08 \text{ BM} \).

\[ \text{[Ni}\text{(_{2}stscN-Ph)}\text{(_2phen)(OH}_{2}\text{)]\cdotH}_{2}\text{O (42)} \]

It was prepared by a method similar to that of complex 39. Color: red (68%, M.p. above 300 °C) Anal. Calcd. for C_{40}H_{30}N_8Ni_2O_5S_2: C, 57.46; H, 3.59; N, 13.41 %. Found: C, 58.79; H, 3.65; N, 12.07 %. IR (KBr, cm^{-1}, selected absorption bands): \( \nu(\text{N–H}) 3424\text{br} \); \( \nu(\text{O–H}) 3374\text{s} \); \( \nu(\text{C–H}) 3051\text{s}, 2959\text{w}, 2924 \); \( \nu(\text{C=N}) + \nu(\text{C=C}) 1597\text{s}, 1545\text{s} \); \( \nu(\text{C–N}) 1030\text{s}, 916\text{s} \); \( \nu(\text{C–S}) 756\text{s} \).

Electronic absorption spectrum (0.5 \times 10^{-4} \text{ M in DMSO, } \lambda_{\text{max}}/\text{nm, } e/\text{L mol}^{-1} \text{ cm}^{-1}): 427 (0.94 \times 10^4), 385 (1.11 \times 10^4), 326 (1.29 \times 10^4), 275 (3.64 \times 10^4), 269 (3.55 \times 10^4). Magnetic moment: \( \mu_{\text{eff}} = 2.97 \text{ BM} \).
To a suspension of \{\text{Ni}(5\text{-Me-hbtscN-Me})\} (0.020 g, 0.071 mmol) in acetonitrile (10 mL) was added phenanthroline (0.007, 0.035 mmol). During stirring period of 4 h, red compound started forming, which was filtered and dried. Crystals for X-ray were grown in methanol and dichloromethane mixture (3:1 : : v/v). The crystals were air sensitive. Color: red (68\%, M.p. 210–212 °C). Anal. Calcd. for C_{35.50}H_{44}N_{8}Ni_{2}O_{5.50}S_{2}: C, 49.98; H, 5.16; N, 13.14 %. Found: C, 50.19; H, 5.46; N, 12.98 %. IR (KBr, cm\(^{-1}\), selected absorption bands): \(\nu\text{(N–H)}\) 3426br; \(\nu\text{(O–H)}\) 3346s; \(\nu\text{(C–H)}\) 3046m, 2927m, 2853w; \(\nu\text{(C=N)} + \nu\text{(C=C)}\) 1584s, 1546s; \(\nu\text{(C–N)}\) 1029s, 951m; \(\nu\text{(C–S)}\) 764s. Electronic absorption spectrum (0.5 × 10^{-4} M in DMSO, \(\lambda_{\text{max}}/\text{nm}, \epsilon/\text{L mol}^{-1}\text{ cm}^{-1}\)): 426 (1.20 × 10^{4}), 382 (1.39 × 10^{4}), 324 (1.47 × 10^{4}), 292 (2.91 × 10^{4}), 279 (4.83 × 10^{4}), 273 (5.50 × 10^{4}), 270 (6.13 × 10^{4}). Fluorescence spectrum: \(\lambda_{\text{max}}^\text{ex} = 340\) nm, \(\lambda_{\text{max}}^\text{em} = 396, 494\) nm. Magnetic moment: \(\mu_{\text{eff}} = 3.07\) BM.

It was prepared by a method similar to that of complex 43. Color: brown-red (67\%, M.p. 215–217 °C). Anal. Calcd. for C_{38.50}H_{50}N_{8}Ni_{2}O_{6}S_{2}: C, 50.87; H, 5.58; N, 12.49 %. Found: C, 51.10; H, 5.46; N, 12.15 %. IR (KBr, cm\(^{-1}\), selected absorption bands): \(\nu\text{(N–H)}\) 3411br; \(\nu\text{(O–H)}\) 3367s; \(\nu\text{(C–H)}\) 2998m, 2925w, 2874m; \(\nu\text{(C=N)} + \nu\text{(C=C)}\) 1587s, 1532s; \(\nu\text{(C–N)}\) 1042s, 951m; \(\nu\text{(C–S)}\) 775s. Electronic absorption spectrum (0.5 × 10^{-4} M in DMSO, \(\lambda_{\text{max}}/\text{nm}, \epsilon/\text{L mol}^{-1}\text{ cm}^{-1}\)): 426 (1.84 × 10^{4}), 385 (1.85 × 10^{4}), 346 (1.69 × 10^{4}), 323 (2.05 × 10^{4}), 292 (3.66 × 10^{4}), 281 (5.40 × 10^{4}), 272 (7.91 × 10^{4}), 262 (7.14 × 10^{4}). Fluorescence spectrum: \(\lambda_{\text{max}}^\text{ex} = 340\) nm, \(\lambda_{\text{max}}^\text{em} = 396, 481\) nm. Magnetic moment: \(\mu_{\text{eff}} = 3.11\) BM.
To suspension of \{Ni(hacptscN-Me)} (0.040 g, 0.143 mmol) in acetonitrile (10 mL) was added phenanthroline (0.013, 0.072 mmol). During stirring period of 2 h, a clear dark red solution was obtained. The filtered solution was kept for crystallization. Crystals for X-ray were grown from this solution.

**Color:** red (71%, M.p. 240–242 °C). Anal. Calcd. for C\textsubscript{64}H\textsubscript{60}N\textsubscript{16}Ni\textsubscript{4}O\textsubscript{4}S\textsubscript{4}: C, 51.93; H, 4.06; N, 15.15 %. Found: C, 52.19; H, 4.26; N, 14.98 %. IR (KBr, cm\textsuperscript{-1}, selected absorption bands): \(\nu\)(N–H) 3427br; \(\nu\)(C–H) 2963m, 2921w, 2866w; \(\nu\)(C=N) + \(\nu\)(C=C) 1596s, 1534s; \(\nu\)(C–N) 1043s, 964s; \(\nu\)(C–S) 754s. Electronic absorption spectrum (0.5 \times 10\textsuperscript{-4} M in DMSO, \(\lambda\)\textsubscript{max}/nm, \(\varepsilon\)/L mol\textsuperscript{-1} cm\textsuperscript{-1}): 419 (0.80 \times 10\textsuperscript{4}), 380 (1.57 \times 10\textsuperscript{4}), 318 (1.59 \times 10\textsuperscript{4}), 301 (1.95 \times 10\textsuperscript{4}), 276 (4.12 \times 10\textsuperscript{4}), 268 (5.21 \times 10\textsuperscript{4}).

**[Ni\textsubscript{4}(hacptscN-Et)\textsubscript{4}(phen)\textsubscript{2}] (46)**

It was prepared by a method similar to that of complex 45. Color: red (65%, M.p. 280–282 °C). Anal. Calcd. for C\textsubscript{68}H\textsubscript{68}N\textsubscript{16}Ni\textsubscript{4}O\textsubscript{4}S\textsubscript{4}: C, 53.11; H, 4.43; N, 14.58 %. Found: C, 52.88; H, 4.13; N, 14.22 %. IR (KBr, cm\textsuperscript{-1}, selected absorption bands): \(\nu\)(N–H) 3447br; \(\nu\)(C–H) 2963m, 2921w, 2866w; \(\nu\)(C=N) + \(\nu\)(C=C) 1595s, 1529s; \(\nu\)(C–N) 1013s; \(\nu\)(C–S) 769s. Electronic absorption spectrum (0.5 \times 10\textsuperscript{-4} M in DMSO, \(\lambda\)\textsubscript{max}/nm, \(\varepsilon\)/L mol\textsuperscript{-1} cm\textsuperscript{-1}): 415 (0.91 \times 10\textsuperscript{4}), 381 (1.59 \times 10\textsuperscript{4}), 319 (1.75 \times 10\textsuperscript{4}), 300 (2.35 \times 10\textsuperscript{4}), 275 (5.29 \times 10\textsuperscript{4}), 266 (6.68 \times 10\textsuperscript{4}).
[Ni(κ^3-O,N^3,S-stscN-Me)(κ^3-N,N,N-terpy)]·H₂O (47)

To a suspension of {Ni(stscN-Me)} (0.020 g, 0.075 mmol) in CH₃OH (10 mL) was added solid terpyridine (0.017 g, 0.075 mmol). The contents were stirred and after a few minutes a clear red solution was formed. During stirring period of 4 h, red compound started forming, which was filtered and dried. Crystals for X-ray were grown in methanol and dichloromethane mixture (1:3 :: v/v). Color: red (65%, M.p. above 300 °C). Anal. Calcd. for C₂₄H₂₃N₆NiO₃S: C, 53.81; H, 4.48; N, 15.69 %. Found: C, 53.97; H, 4.42; N, 15.35 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N–H) 3411br; ν(C–H) 3056m, 2927m, 2827w; ν(C=N) + ν(C=C) 1593s, 1480s; ν(C–N) 1013s, 939s; ν(C–S) 769s. Electronic absorption spectrum (10⁻³ / 0.5×10⁻⁴ M in DMSO, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 542 (0.16 × 10³), 420 (0.99 × 10⁴), 400 (0.97 × 10⁴), 380 (0.81 × 10⁴), 361 (0.71 × 10⁴), 341 (1.03 × 10⁴), 321 (1.81 × 10⁴), 313 (1.79 × 10⁴), 283 (2.41 × 10⁴), 278 (2.41 × 10⁴), 266 (2.29 × 10⁴). Fluorescence spectrum: λ_max^ex = 320 nm, λ_max^em = 384, 481 nm; λ_max^ex = 340 nm, λ_max^em = 378, 478 nm. Magnetic moment: μ_eff = 2.99 BM.

2[Ni(κ^3-O,N^3,S-stscN-Ph)(κ^3-N,N,N-terpy)]·H₂O (48)

It was prepared by a method similar to that for complex 47. Color: red-brown (65%, M.p. above 300 °C). Anal. Calcd. for C₅₈H₄₆N₁₂Ni₂O₃S₂: C, 61.02; H, 4.03; N, 14.73 %. Found: C, 59.88; H, 4.27; N, 14.99 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3428br; ν(C–H) 3011m, 2923m, 2878w; ν(C=N) + ν(C=C) 1599s, 1530s; ν(C–N) 1023m; ν(C–S) 771s. Electronic absorption spectrum (10⁻³ / 0.5 × 10⁻⁴ M in DMSO, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 529 (0.22 × 10³), 432 (0.62 × 10⁴), 383 (0.81 × 10⁴), 340 (1.10 × 10⁴), 326 (1.41 × 10⁴), 317 (1.38 × 10⁴), 283 (2.24 × 10⁴), 277 (2.24 × 10⁴), 264 (1.92 × 10⁴). Magnetic moment: μ_eff = 2.92 BM.
[Ni(κ³-O,N³,S-5-OMe-hbtscN-Me)(κ³-N,N,N-terpy)] (49)

It was prepared by a method similar to that for complex 47. Color: red-brown (67%, M.p. above 300 °C). Anal. Calcd. for C₂₅H₂₂N₆NiO₂S₂: C, 56.68; H, 4.16; N, 15.87 %. Found: C, 56.42; H, 4.39; N, 15.62 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N⁻H) 3432br; ν(C–H) 3034m, 2956m, 2878w; ν(C=N) + ν(C=C) 1590s, 1480s; ν(C–N) 1027s, 921s; ν(C–S) 775s.

Electronic absorption spectrum (10⁻³ / 10⁻⁴ M in DMSO, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 549 (0.29 × 10⁻³), 431 (0.92 × 10⁻⁴), 372 (0.72 × 10⁻⁴), 334 (1.27 × 10⁻⁴), 313 (2.07 × 10⁻⁴), 303 (1.99 × 10⁻⁴), 276 (2.78 × 10⁻⁴), 260 (2.77 × 10⁻⁴). Fluorescence spectrum: λ_maxex = 320 nm, λ_maxem = 418 nm; λ_maxex = 340 nm, λ_maxem = 418 nm; λ_maxex = 350 nm, λ_maxem = 418 nm; λ_maxex = 380 nm, λ_maxem = 418 nm. Magnetic moment: μ_eff = 2.95 BM.

[Ni₂(κ³-O,N³,S-stscN-Me)₂(μ-P,P-dppm)] (50)

It was prepared by a method similar to that for complex 21. Color: red (58%, M.p. 210–212 °C). Anal. Calcd. for C₄₃H₄₀Ni₂N₆O₂P₂S₂: C, 59.48; H, 4.61; N, 9.68 %. Found: C, 59.18; H, 4.89; N, 9.56 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N⁻H) 3412s; ν(C–H) 3049w, 2991w, 2927w, 2878m; ν(C=N) + ν(C=C) 1600s, 1541s; ν(P–C_ph) 1097s; ν(C–N) 1026s, 989s, 916s; ν(C–S) 752s. ¹H NMR (δ, ppm; CDCl₃): δ = 8.21 (2H, d, C₂H), 7.80 (4H, m, C⁵H+C⁶H), 7.15 (20H, m, α- + p- + m-H_ph), 6.54 (4H, m, C⁸H + C⁷H), 4.91 (2H, db, N¹H), 2.86 (2H, s, CH₂), 2.10 (6H, d, CH₃(N¹) ppm. ³¹P NMR (δ, ppm; CDCl₃): δ = 30.23 ppm; coordination shift, Δδ (δ_complex−δ_dppm) = 34.93 ppm.
It was prepared by a method similar to that for complex 50. Color: red (60%, M.p. 215–217 °C). Anal. Calcd. for C_{45}H_{44}Ni_{2}N_{6}O_{2}P_{2}S_{2}: C, 57.18; H, 4.66; N, 8.89 %. Found: C, 56.98; H, 4.45; N, 9.01 %. IR (KBr, cm^{-1}, selected absorption bands): v(N-H) 3419s; v(C-H) 3078w, 2963w, 2927w, 2867m; v(C=N) + v(C=C) 1600s, 1541s; v(P-C) 1097s; v(C-N) 1045s, 1027s, 999s; v(C-S) 764s. \(^{1}\)H NMR (\(\delta\), ppm; CDCl\(_3\)): \(\delta = 7.99 (6H, m, C_{2}H + C_{5}H + C_{6}H), 6.50 (4H, m, C_{8}H + C_{7}H), 4.43 (2H, db, N_{1}H), 3.27 (4H, m, CH_{2}(N_{1})), 2.01 (2H, s, CH_{2}), 1.14 (6H, d, CH_{3}(N_{1})) \text{ppm.} \(^{31}\)P NMR (\(\delta\), ppm; CDCl\(_3\)): \(\delta = 30.41 \text{ ppm; coordination shift, } \Delta \delta (\delta_{\text{complex}}-\delta_{\text{dppm}}) = 35.11 \text{ ppm.}

It was prepared by a method similar to that for complex 50. Color: red (59 %, M.p. 180–182 °C). Anal. Calcd. for C_{55}H_{47}Ni_{2}N_{7}O_{2}P_{2}S_{2}: C, 61.09; H, 4.35; N, 9.07 %. Found: C, 69.24; H, 4.49; N, 8.87 %. IR (KBr, cm^{-1}, selected absorption bands): v(N-H) 3433br; v(C-H) 3052m, 2998w; v(C=N) + v(C=C) 1602s, 1535s; v(P-C) 1097s; v(C-N) 1020s, 996s, 902w; v(C-S) 745s. \(^{1}\)H NMR (\(\delta\), ppm; CDCl\(_3\)): \(\delta = 8.20 (2H, s, C_{2}H), 7.96 (12H, m, o-H_{ph}), 7.48 (6H, s, p-H_{ph}), 7.24 (12H, s, m-H_{ph} + CDCl\(_3\)), 7.14 (1H, s, C_{5}H), 6.94 (1H, s, C_{6}H), 6.52 (1H, s, C_{8}H + C_{7}H), 6.45 (1H, sb, N_{1}H), 3.21(2H, s, CH_{2}). \(^{31}\)P NMR (\(\delta\), ppm; CDCl\(_3\)): \(\delta = 13.50 \text{ ppm; coordination shift, } \Delta \delta (\delta_{\text{complex}}-\delta_{\text{dppm}}) = 36.06 \text{ ppm.} \)
[Ni(κ⁢³-O,N⁢³,S-hacptscN-Me)(κ¹-P-dppm)] (53)

To a light yellow solution of H₂hacptscN-Me (0.022 g, 0.100 mmol) in CH₃CN (10 mL) was added solid Ni(OAc)₂ (0.025 g, 0.100 mmol) and stirred for 2 h. During stirring rust compound get separated. To this was added solid dppm (0.034 g, 0.100 mmol) and stirred for 15 min. The color of the solution changed to reddish brown. The solution was filtered and kept for crystallization. Slow evaporation of the solution formed sticky mass, which was crystallized in methanol. Color: red-brown (59 %, M.p. 176–178 °C). IR (KBr, cm⁻¹, selected absorption bands): ν(N=H) 3420 br; ν(C–H) 3051 m, 2925 m, 2856 w; ν(C=N) + ν(C=C) 1542 s, 1483 s; ν(P–C) 1099 s; ν(C–N) 1068 s, 1025 m, 915 s; ν(C–S) 758 s.

¹H NMR (δ, ppm; CDCl₃): = 7.95 (8H, s, o–Hₘₜₜ), 7.82 (4H, s, p–Hₘₜₜ), 7.72 (8H, t, m–Hₘₜₜ), 6.97 (2H, s, C₅H + C₆H), 4.42 (1H, sb, N₁H), 3.45 (2H, d, CH₂), 2.88 (3H, s, CH₃(C₂)), 2.71 (3H, s, CH₃(N₁)) ppm.

³¹P NMR (δ, ppm; CDCl₃): δ = 12.42, -26.48 ppm; coordination shift, δ(δcomplex–δdppm) = 34.94, -3.92 ppm.

[Ni(κ³-O,N³,S-hacptscN-Et)(κ¹-P-dppm)] (54)

It was prepared by a method similar to that for complex 53. Color: red-brown (59 %, M.p. 198–200 °C). Anal. Calcd. for C₃₆H₃₅NiN₃O₂P₂S: C, 63.68; H, 5.16; N, 6.19 %. Found: C, 63.97; H, 4.98; N, 6.27 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N=H) 3451 br; ν(C–H) 3043 m, 2927 m, 2878 w; ν(C=N) + ν(C=C) 1548 s, 1480 s; ν(P–C) 1100 s; ν(C–N) 1068 s, 1024 s. ᵱH NMR (δ, ppm; CDCl₃): δ = 7.81 (1H, dd, C⁵H), 7.58 (1H, dd, C⁶H), 7.27 (20H, m, o– + p– + m–Hₘₜₜ), 6.59 (1H, m, C⁷H), 6.45 (1H, dd, C⁷H), 4.48 (1H, sb, N¹H), 3.30 (2H, m, CH₂(N¹)), 3.17 (2H, d, CH₂), 2.73 (3H, s, CH₃(C²)), 1.15 (6H, t, CH₃(N¹)) ppm. ᵱ³¹P NMR (δ, ppm; CDCl₃): δ = 35.51, -7.17 ppm; coordination shift, Δδ(δcomplex–δdppm) = 40.21, -2.47 ppm.
To a light green solution of NiCl$_2$·6H$_2$O salt (0.025 g, 0.105 mmol) in CH$_3$CN was added solid H$_2$ptscN-Me (0.018 g, 0.105 mmol) followed by the addition of Et$_3$N base (1mL) and stirred for 6h. Brown colored compound get separated during stirring alongwith the formation of Et$_3$NH$^+Cl^-$ salt. This compound was filtered and dried.

Analytical data supported the formation of complex of stoichiometry, \{Ni(ptscN-Me)\} \{Anal.Calcd for C$_7$H$_8$NiN$_4$S: C, 35.19; H, 3.35; N, 23.46 %; Found: C, 34.93; H, 4.31; N, 23.84 \%\}. To a suspension of \{Ni(ptscN-Me)\} (0.025 g, 0.111 mmol) in acetonitrile was added pyridine (0.5 cm$^3$) and stirred till clear solution was obtained. The slow evaporation of this solution gave black crystals. Color: black (75 %, M.p. 240–242 °C). Anal. Calcd. for C$_{14}$H$_{18}$N$_8$NiS$_2$: C, 39.89; H, 4.27; N, 26.59 %. Found: C, 40.12; H, 4.22; N, 26.78 %. $^1$H NMR data ($\delta$, ppm; CDCl$_3$): $\delta$ = 11.13 (2H, sb, N$_4$H), 7.22 (2H, s, C$_2$H), 6.96 (2H, s, C$_6$H), 6.53 (2H, t, C$_4$H), 6.22 (2H, dd, C$_5$H), 4.90 (2H, s, N$_1$HMe), 2.98 (6H, d, CH$_3$) ppm.

To a suspension of \{Ni(ptscN-Me)\} (0.025 g, 0.111 mmol) in acetonitrile was added solid bipyridine (0.17, 0.111) and stirred till clear solution was obtained. The slow evaporation of this solution gave red-brown crystals. Color: red-brown (73 %, M. p. 160 – 162 °C). Anal. Calcd. for C$_{24}$H$_{26}$N$_{10}$NiS$_2$: C, 49.88; H, 4.50; N, 24.25 %. Found: C, 50.02; H, 4.42; N, 24.43 %. IR (KBr, cm$^{-1}$, selected absorption bands): \(\nu(N^1–H)\) 3421br; \(\nu(N^4–H)\) 3317s; \(\nu(C–N)\) 1018s, 963s; \(\nu(C–S)\) 762s. Electronic absorption spectrum (0.5 × 10$^{-4}$ M in DMSO, $\lambda_{max}$/nm, $\epsilon$/L mol$^{-1}$ cm$^{-1}$): 413 (0.96 × 10$^4$), 374 (1.89 × 10$^4$), 353 (2.14 × 10$^4$), 333 (2.01 × 10$^4$), 307 (1.68 × 10$^4$), 294 (2.00 × 10$^4$), 275 (2.50 × 10$^4$). Magnetic moment: $\mu_{eff}$ = 2.98 BM.
To trans-PdCl₂(PPh₃)₂ precursor (0.050 g, 0.071 mmol) suspended in toluene (15 mL) was added solid H₂atttscN-Me (0.014 g, 0.071 mmol), followed by the addition of Et₃N base (1 mL). The mixture was stirred for 3 h during which a clear red solution was formed along with Et₃NH⁺Cl⁻, separating in solution at the bottom of the flask. The solution was filtered to remove Et₃NH⁺Cl⁻ and allowed to evaporate at room temperature. After evaporation, red colored sticky mass was crystallized from dichloromethane and methanol (3:1 :: v/v). Color: red (68%, M.p. 265–267 °C). Anal. Calcd. for C₂₆H₂₄N₃PPdS: C, 53.80; H, 4.14; N, 7.24 %. Found: C, 53.54; H, 4.27; N, 7.31 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹⁻H) 3414br; ν(C–H) 3040m, 2942m, 2878w; ν(C=N) + ν(C=C) 1567m, 1508s; ν(P–Cₚₚ) 1099s; ν(C–N) 1021s, 996sh, 867s; ν(C–S) 759s. ¹H NMR (δ, ppm; CDCl₃): δ = 7.58 (6H, m, o-Hₚₚ), 7.40 (9H, m, p- + m-Hₚₚ), 6.78 (1H, d, C⁵H), 5.79 (1H, d, C⁶H), 4.65 (1H, sb, N¹H), 2.92 (3H, d, CH₃(C²)), 2.36 (3H, s, CH₃(N¹)) ppm. ³¹P NMR (δ, ppm; CDCl₃): δ = 40.41 ppm; coordination shift, Δδ (δ_{complex}–δ_{PPh₃}) = 45.10 ppm.

It was prepared by a method similar to that for complex 56. Color: red (70%, M.p. 215–217 °C). Anal. Calcd. for C₃₁H₂₆N₃PPdS: C, 57.94; H, 4.05; N, 6.54 %. Found: C, 57.89; H, 4.11; N, 6.52 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹⁻H) 3385br; ν(C–H) 3053m, 2989m; ν(C=N) + ν(C=C) 1593m, 1493s; ν(P–Cₚₚ) 1108s; ν(C=N) 1021s, 996sh, 867s; ν(C–S) 768s. ¹H NMR (δ, ppm; CDCl₃): δ = 7.64 (8H, m, o-Hₚₚ), 7.55 (4H, m, p-Hₚₚ), 7.43 (8H, m, m-Hₚₚ), 6.92 (1H, q, C⁵H), 5.83 (1H, d, C⁶H), 6.64 (1H, sb, N¹H), 2.45 (3H, d, CH₃(C²)) ppm. ³¹P NMR (δ, ppm; CDCl₃): δ = 40.28, 33.34 ppm; coordination shift, Δδ (δ_{complex}–δ_{PPh₃}) = 44.98, 38.04 ppm.
[Pd(κ^3-C,N^3,S-acptscN-Me)(κ^1-P-PPh_3)] (58)

To trans-PdCl_2(PPh_3)_2 precursor (0.050 g, 0.071 mmol) suspended in acetonitrile (15 mL) was added solid H_2acptscN-Me (0.015 g, 0.071 mmol), followed by the addition of Et_3N base (1mL). The mixture was stirred for 3 h during which a clear orange solution was formed. The solution was filtered and allowed to evaporate at room temperature. Yellow colored crystals were formed along with Et_3NH^+Cl^-, separating in solution at the bottom of the flask. Color: orange (67%, M.p. 240–242 °C). Anal. Calcd. for C_{28}H_{26}N_{3}PPdS: C, 58.54; H, 4.53; N, 7.32 %. Found: C, 58.50; H, 4.57; N, 7.29 %. IR (KBr, cm\(^{-1}\), selected absorption bands): ν(N^1–H) 3412br; ν(C–H) 3047m, 2908m; ν(C=N) + ν(C=C) 1572m, 1504s; ν(P–C_{ph}) 1097s; ν(C–N) 1062s, 1013m, 825m; ν(C–S) 751s. \(^1\)H NMR (δ, ppm; CDCl_3): δ = 7.68 (6H, m, o-H_{ph}), 7.40 (10H, m, p-H_{ph} +m-H_{ph}+C^5H), 7.07 (1H, dd, C^8H), 6.85 (1H, tb, C^6H), 6.30 (1H, qd, C^7H), 4.64 (1H, sb, N^1H), 2.91 (3H, d, CH_3(C^2)), 2.39 (3H, s, CH_3(N^1)) ppm. \(^{31}\)P NMR(δ, ppm; CDCl_3): δ 39.13 ppm; coordination shift, Δδ (δ_{complex}–δ_{PPh_3}) = 43.83 ppm.

[Pd(κ^3-C,N^3,S-acptscN-Ph)(κ^1-P-PPh_3)] (59)

It was prepared by a method similar to that for complex 58. Color: orange (67%, M.p. 260–262 °C). Anal. Calcd. for C_{33}H_{28}N_{3}PPdS: C, 62.26; H, 4.40; N, 6.60 %. Found: C, 62.31; H, 4.37; N, 6.56 %. IR (KBr, cm\(^{-1}\), selected absorption bands): ν(N^1–H) 3420br; ν(C–H) 3112m, 3020m; ν(C=N) + ν(C=C) 1599s, 1543s; ν(P–C_{ph}) 1098s; ν(C–N) 1062s, 1013m, 825m; ν(C–S) 758s. \(^1\)H NMR (δ, ppm; CDCl_3): δ = 7.75 (8H, m, o-H_{ph}), 7.40 (15H, m, p-H_{ph}+m-H_{ph}+C^5H), 7.07 (1H, dd, C^8H), 6.85 (1H, tb, C^6H), 6.30 (1H, qd, C^7H), 4.64 (1H, sb, N^1H), 2.91 (3H, d, CH_3(C^2)) ppm. \(^{31}\)P NMR (δ, ppm; CDCl_3): δ = 38.32 ppm; coordination shift, Δδ (δ_{complex}–δ_{PPh_3}) = 43.79 ppm.
[Pd(κ3-C,N3,S-bzptscN-Me)(κ1-P-PPh3)] (60)

It was prepared by a method similar to that for complex 58. Color: orange (70%, M.p. 252–254 °C). Anal. Calcd. for C31H29N3PPdS: C, 58.45; H, 4.55; N, 6.59 %. Found: C, 58.45; H, 4.49; N, 6.63 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹-H) 3409br; ν(C–H) 3013m, 2965m, 2889m; ν(C=N) + ν(C=C) 1525s, 1497s; ν(P–C) 1097sh; ν(C–N) 1034s, 916sh; ν(C–S) 770s. 1H NMR (δ, ppm; CDCl₃): δ = 7.72 (6H, m, o-Hₚₜₚ), 7.40 (15H, m, p- + m-Hₚₜₚ + C⁵,₈H, C⁴⁺,₅⁺,₈⁺H), 6.73 (2H, d, C⁷H + C⁷'H), 6.45 (1H, q, C⁶H), 6.34 (1H, q, C⁶'H), 4.70 (1H, sb, N¹H), 2.70 (3H, d, CH₃(C²)) ppm. 3¹P NMR (δ, ppm; CDCl₃): δ = 39.26 ppm; coordination shift, Δδ (δ(κ₃-PPh₃) – δ(κ₃-PPh₃)) = 43.96 ppm.

[Pt(κ3-C,N3,S-bzptscN-Ph)(κ1-P-PPh3)] (61)

It was prepared by a method similar to that for complex 58. Color: orange (71%, M.p. 270–272 °C). Anal. Calcd. for C₃₆H₃₁N₃PPdS: C, 61.08; H, 4.43; N, 6.01 %. Found: C, 61.11; H, 4.39; N, 5.98 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹-H) 3405br; ν(C–H) 3015m, 2983m; ν(C=N) + ν(C=C) 1530s, 1508s; ν(P–C) 1098sh; ν(C–N) 1035s, 897m; ν(C–S) 761s. 1H NMR (δ, ppm; CDCl₃): δ = 7.72 (6H, m, o-Hₚₜₚ), 7.40 (15H, m, p- + m-Hₚₜₚ + C⁵,₈H, C⁴⁺,₅⁺,₈⁺H), 6.83 (2H, d, C⁷H + C⁷'H), 6.45 (1H, q, C⁶H), 6.34 (1H, q, C⁶'H), 4.70 (1H, sb, N¹H), 2.70 (3H, d, CH₃(C²)) ppm. 3¹P NMR (δ, ppm; CDCl₃): δ = 39.12 ppm; coordination shift, Δδ (δ(κ₃-PPh₃) – δ(κ₃-PPh₃)) = 44.59 ppm.

[Pd(κ3-N₄,N₃,S-aptscN-Me)(κ1-P-PPh3)] (62)

It was prepared by a method similar to that for complex 56. Color: red (69%, M.p. 248–250 °C). Anal. Calcd. for C₂₆H₂₅N₄PPdS: C, 55.42; H, 4.44; N, 9.95 %. Found: C, 55.39; H, 4.49; N, 9.98 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹-H) 3422br; ν(C–H) 3077m, 2945m, 2897w; ν(C=N) + ν(C=C) 1532s, 1497s; ν(P–C) 1099s; ν(C–N) 1030s, 813; ν(C–S) 751s. 1H NMR (δ, ppm; CDCl₃): δ = 7.65 (6H, m, o-Hₚₜₚ), 7.42 (9H, m, p- + m-Hₚₜₚ), 6.47 (1H,
dd, C\(^6\)H), 5.78 (1H, q, C\(^4\)H), 5.63 (1H, q, C\(^5\)H), 4.53 (1H, sb, N\(^1\)H), 2.89 (3H, d, CH\(_3\)(C\(^2\))), 2.35 (3H, s, CH\(_3\)(N\(^1\))) ppm. \(^3\)P NMR (\(\delta\), ppm; CDCl\(_3\)): \(\delta = 34.84\) ppm; coordination shift, \(\Delta\delta (\delta_{\text{complex}} - \delta_{\text{PPh}_3}) = 39.54\) ppm.

\([\text{Pd}(\kappa^3-N^4,N^3,S-\text{atscN-Me})_2\text{Cl}(\text{PPh}_3)_2]\) (63)

It was prepared by a method similar to that for complex 56. Color: red (71%, M.p. 270–272 °C). Anal. Calcd. for C\(_{31}\)H\(_{27}\)N\(_4\)PPdS: C, 59.52; H, 4.32; N, 8.96 %. Found: C, 59.48; H, 4.37; N, 9.01 %. IR (KBr, \(\text{cm}^{-1}\), selected absorption bands): \(\nu(\text{N}^1-H)\) 3396br; \(\nu(\text{C}-\text{H})\) 3051s, 2997m; \(\nu(\text{C} = \text{N}) + \nu(\text{C} = \text{C})\) 1619s, 1480s; \(\nu(\text{P} - \text{C}_{\text{ph}})\) 1096s; \(\nu(\text{C} - \text{N})\) 999s, 825s; \(\nu(\text{C} - \text{S})\) 767s.

\(^1\)H NMR (\(\delta\), ppm; CDCl\(_3\)): \(\delta = 7.68\) (8H, m, o-H\(_{\text{ph}}\)), 7.53 (12H, m, \(p- + m\)-H\(_{\text{ph}}\)), 6.90 (1H, t, C\(^6\)H), 6.54 (1H, d, C\(^4\)H), 6.64 (1H, sb, N\(^1\)H), 5.70 (1H, dd, C\(^5\)H), 2.47 (3H, d, CH\(_3\)(C\(^2\)))) ppm.

\(^3\)P NMR (\(\delta\), ppm; CDCl\(_3\)): \(\delta = 28.73\) ppm; coordination shift, \(\Delta\delta (\delta_{\text{complex}} - \delta_{\text{PPh}_3}) = 34.20\) ppm.

\([\text{Pd}(\kappa^3-N^4,N^3,S-\text{atscN-Me})_2\text{Cl}(\text{PPh}_3)_2]\) (64)

To trans-PdCl\(_2\)(PPh\(_3\))\(_2\) precursor (0.050 g, 0.071 mmol) suspended in toluene (15 mL) was added solid HaftscN-Me (0.014 g, 0.071 mmol), followed by the addition of Et\(_3\)N base (1mL). The mixture was stirred for 3 h during which a clear light orange solution was formed along with Et\(_3\)NH\(^+\)Cl\(^-\), separating in solution at the bottom of the flask. The solution was filtered to remove Et\(_3\)NH\(^+\)Cl\(^-\) and allowed to evaporate at room temperature. After evaporation, orange colored sticky mass was obtained. This mass was crystallized in a mixture of acetone and methanol (3:1 :: v/v). During slow evaporation of solvent, an unstable product of stoichiometry, [Pd(afscN-Me)Cl(PPh\(_3\))] \{Anal.Calcd for C\(_{24}\)H\(_{23}\)PdN\(_3\)OSP: C, 48.00; H, 4.17; N, 7.00 %; Found: C, 48.51; H, 4.02; N, 7.08 %\} was formed. This compound in solution gets slowly converted into a more stable compound. This reaction involves in situ generation of ligand, 2-hydroxyacetaldehyde-N-methyl thiosemicarbazone (H\(_2\)actscN-Me). Color: orange (65%, M.p. 215–217 °C). Found: C, 44.12; H, 3.98; N, 7.35; C\(_{44}\)H\(_{44}\)N\(_6\)Cl\(_2\)O\(_2\)P\(_2\)Pd\(_3\)S\(_2\) requires: C, 43.82; H, 3.65; N, 6.97 (%). IR bands (KBr pellets, \(\text{cm}^{-1}\)) \(\nu(\text{N}^1-H)\) 3427br; \(\nu(\text{C} - \text{H})\) 3053m, 2927m, 2885m; \(\nu(\text{C} - \text{N}) + \nu(\text{C} = \text{C})\) 1547s, 1434s;
ν(P–C₉H₅) 1097s; ν(C–N) 1071m, 997w; ν(C–S) 743s. ¹H NMR (δ, ppm; CDCl₃): δ = 7.78–7.37 (30H, m, o- + p- + m-Ph), 3.79d (2H, d, N¹H), 2.64d (6H, d, CH₃(C²)), 2.27s (6H, s, CH₃(N¹)) ppm. ³¹P NMR (δ, ppm; CDCl₃): δ = 31.76, 27.00 ppm; coordination shift, Δδ (δ_complex–δ_PPh₃) = 36.46, 31.70 ppm.

[Cu(κ³-O,N³,S-stscN-Me)(κ¹-N-py)] (65)

To a solution of H₂stscN-Me (0.026 g, 0.125 mmol) in methanol was added solid Cu(OAc)₂ salt (0.025 g, 0.125 mmol) and stirred. The brown colored precipitates formed during stirring were filtered and allowed to dry at room temperature. The analytical data supported the formation of compound of empirical composition, {Cu(stscN-Me)} {Anal.Calcd for C₉H₉CuN₃OS: C, 39.92; H, 3.33; N, 15.52 %; Found: C, 40.09; H, 3.27; N, 15.71 %}. To a suspension of {Cu(stscN-Me)} (0.025 g, 0.094 mmol) in acetonitrile was added pyridine (0.5 cm³), and contents were stirred for 1 h. The color of the solution was changed from brown to red. The clear solution obtained was allowed to evaporate at room temperature which yielded red colored crystals. Color: red (62%, M.p. 244–246 °C). Anal. Calcd. for C₁₄H₁₄N₄CuOS: C, 48.01; H, 4.00; N, 16.00 %; Found: C, 48.30; H, 4.23; N, 15.96 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3423br; ν(C–H) 3081w, 3018w, 2977w, 2883w; ν(C=N) + ν(C=C) 1600s, 1558s; ν(C–N) 1070s, 1028s, 912s; ν(C–S) 756s. Electronic absorption spectrum (10⁻⁴ M in MeOH, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 397 (1.32 × 10⁴), 327 (1.90 × 10⁴), 293 (2.49 × 10⁴). Magnetic moment, μ_eff = 1.80 BM.

[Cu(κ³-O,N³,S-stscN-Ph)(κ¹-N-py)] (66)

It was prepared by a method similar to that for complex 65. Color: red (58%, M.p. 212–214 °C). Anal. Calcd. for C₁₉H₁₆CuN₄OS: C, 55.40; H, 3.89; N, 13.61 %. Found: C, 55.67; H, 3.64; N, 13.53 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3419br, ν(C–H) 3045s, 2988w; ν(C=N) + ν(C=C) 1610s, 1533s, ν(C–N) 1067s, 1022s, 946s; ν(C–S) 749s. Electronic absorption spectrum (10⁻⁴ M in DMSO, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 393 (1.52 × 10⁴), 318 (2.10 × 10⁴), 288 (2.25 × 10⁴). Magnetic moment, μ_eff = 1.82 BM.
[Cu(κ³-O,N³,S-stscN-Me)(κ²-N,N-bipy)]·H₂O (67)

To a suspension of {Cu(stscN-Me)} (0.010 g, 0.037 mmol) in acetonitrile was added solid bipyridine (0.007 g, 0.037 mmol), and contents were stirred for 1 h. The clear reddish green solution obtained was allowed to evaporate at room temperature which yielded red-green needles. Color: green (66%, M.p. 198–200 °C). Anal. Calcd. for C₂₁H₁₇CuN₅OS: C, 56.63; H, 3.82; N, 15.73 %. Found: C, 56.46; H, 4.01; N, 15.62 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3436br; ν(C–H) 3056w, 2957m, 2924w, 2891m; ν(C=N) + ν(C=C) 1534s, 1489s; ν(C–N) 1032s, 971w; ν(C–S) 762s. Electronic absorption spectrum (10⁻³ / 10⁻⁴ M in DMSO, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 576 (0.264 × 10³), 391 (1.46 × 10⁴), 377 (1.38 × 10⁴), 354 (1.07 × 10⁴), 325 (1.91 × 10⁴), 316 (1.82 × 10⁴), 275 (1.47 × 10⁴). Fluorescence spectrum: λ_max² = 340 nm, λ_max⁰ = 406 nm. Magnetic moment, μ_eff = 1.79 BM.

[Cu₂(stscN-Et)₂(bipy)] (68)

It was prepared by a method similar to that for 67. Color: black (66%, M.p. 245–247 °C). Anal. Calcd. for C₃₀H₃₀Cu₂N₈O₂S₂: C, 49.60; H, 4.13; N, 15.43 %. Found: C, 50.06; H, 4.22; N, 15.49 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N¹–H) 3439br; ν(C–H) 3056m, 2977m, 2925m, 2854m; ν(C=N) + ν(C=C) 1545s, 1475s; ν(C–N) 1053m, 928w; ν(C–S) 751s. Electronic absorption spectrum (10⁻³ / 10⁻⁴ M in MeOH, λ_max/nm, ε/L mol⁻¹ cm⁻¹): 572 (0.21 × 10³), 392 (1.06 × 10⁴), 377 (0.99 × 10⁴), 325 (1.34 × 10⁴), 316 (1.29 × 10⁴), 279 (1.64 × 10⁴). Fluorescence spectrum: λ_max² = 340 nm, λ_max⁰ = 442 nm. Magnetic moment, μ_eff = 1.81 BM.
To a suspension of \{\text{Cu(stscN-Me)}\} (0.010 g, 0.037 mmol) in acetonitrile was added \text{phen} (0.007 g, 0.037 mmol), and contents were stirred for 1 h. The clear reddish green solution obtained was allowed to evaporate at room temperature which yielded green needles. Color: green (66\%, M.p. 205–207 °C). Anal. Calcd. for C_{21}H_{19}CuN_{5}O_{2}S: C, 53.79; H, 4.06; N, 14.94 %. Found: C, 53.96; H, 4.21; N, 15.15 %. IR (KBr, cm\(^{-1}\), selected absorption bands): \nu(N–H) 3413br; \nu(C–H) 3042m, 2922m, 2853m, \nu(C=\text{N}) + \nu(C=\text{C}) 1597s, 1493s, \nu(C–N) 1028m, 913w; \nu(C–\text{S}) 765s. Electronic absorption spectrum (10\(^{-3}\) / 10\(^{-4}\) M in DMSO, \(\lambda_{\text{max}}/\text{nm}, \epsilon /\text{L mol}^{-1} \text{cm}^{-1}\)): 579 (0.15 \times 10^3), 508 (0.23 \times 10^3), 394 (0.77 \times 10^4), 376 (0.70 \times 10^4), 323 (1.00 \times 10^4), 313 (0.95 \times 10^4), 280 (1.52 \times 10^4), 264 (2.05 \times 10^4). Magnetic moment, \(\mu_{\text{eff}} = 1.80\) BM.

It was prepared by a method similar to that for 69. Color: red (61\%, M.p. 220–222 °C). Anal. Calcd. for C_{22}H_{23}CuN_{5}OS: C, 52.75; H, 4.60; N, 13.98 %. Found: C, 53.01; H, 4.54; N, 14.02 %. IR (KBr, cm\(^{-1}\), selected absorption bands): \nu(N–H) 3425br; \nu(C–\text{H}) 2989w, 2929m, 2855w; \nu(C=\text{N}) + \nu(C=\text{C}) 1597s, 1518s; \nu(C–N) 1073s, 1045s, 914w; \nu(C–\text{S}) 759s. Electronic absorption spectrum (10\(^{-3}\) / 10\(^{-4}\) M in DMSO, \(\lambda_{\text{max}}/\text{nm}, \epsilon /\text{L mol}^{-1} \text{cm}^{-1}\)): 580 (0.15 \times 10^3), 507 (0.25 \times 10^3), 396 (0.94 \times 10^4), 375 (0.84 \times 10^4), 326 (1.26 \times 10^4), 312 (1.19 \times 10^4), 264 (2.96 \times 10^4). Fluorescence spectrum: \(\lambda_{\text{max}}^{\text{ex}} = 320\) nm, \(\lambda_{\text{max}}^{\text{em}} = 386\) nm. Magnetic moment, \(\mu_{\text{eff}} = 1.83\) BM.
[Cu(κ^3-O,N^3,S-stscN-Me)(κ^2-N,N-tmphen)]·0.11(C_6H_{24}O_6)·2(H_2O) (71)

To a suspension of {Cu(stscN-Me)} (0.010 g, 0.037 mmol) in acetonitrile was added tmphen (0.008 g, 0.037 mmol), and contents were stirred for 1 h. The clear red solution obtained was allowed to evaporate at room temperature which yielded red compound. This compound was crystallized from a mixture of dichloromethane and methanol (3:1 v:v). Color: red (73%, M.p. 212–214 °C). Anal. Calcd. for C_{25.66}H_{31.64}CuN_{5.66}O_{3.66}S: C, 54.57; H, 5.61; N, 12.40 %. Found: C, 54.46; H, 5.64; N, 12.26 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N–H) 3392s, ν(C–H) 3012m, 2950w, 2920m, 2850w; ν(C=N) + ν(C=C) 1618s, 1586s, ν(C–N) 1078s, 1027s, 953s, ν(C–S) 767s. Electronic absorption spectrum (10⁻³ / 10⁻⁴ M in DMSO, λ_{max}/nm, ε/L mol⁻¹ cm⁻¹): 574 (0.19 × 10³), 394 (1.14 × 10⁴), 378 (1.06 × 10⁴), 324 (1.46 × 10⁴), 310 (1.50 × 10⁴), 274 (2.95 × 10⁴). Magnetic moment, μ_{eff} = 1.80 BM.

[Cu(κ^3-O,N^3,S-stscN-Et)(κ^2-N,N-tmphen)] (72)

It was prepared by a method similar to that for 71. Color: red (69%, M.p. 235–237 °C). Anal. Calcd. for C_{26}H_{27}CuN_{5}O_{3}S: C, 59.73; H, 5.17; N, 13.40 %. Found: C, 60.01; H, 5.47; N, 13.09 %. IR peaks (KBr, cm⁻¹): ν(N–H) 3446br; ν(C–H) 2997m, 2958w, 2924m, 2854w; ν(C=N) + ν(C=C) 1599s, 1488s; ν(C–N) 1068s, 1016s, 917s; ν(C–S) 767s. Electronic absorption spectrum (10⁻³ / 10⁻⁴ M in DMSO, λ_{max}/nm, ε/L mol⁻¹ cm⁻¹): 579 (0.11 × 10⁴), 505 (0.24 × 10⁴), 389 (0.985 × 10⁴), 324 (1.31 × 10⁴), 309 (1.57 × 10⁴), 273 (3.84 × 10⁴), 270 (3.72 × 10⁴). Fluorescence spectrum: λ_{max}^ex = 320 nm, λ_{max}^em = 394 nm. Magnetic moment, μ_{eff} = 1.82 BM.
To a light yellow solution of HftscN-Me (0.022 g, 0.294 mmol) in methanol (10 mL) was added copper(II) chloride (0.025 g, 0.147 mmol) followed by stirring for 1 h. During stirring, green precipitation took place. Upon refluxing this for 1 h, yellow crystalline compound was separated, which was crystallized from a mixture of dichloromethane and acetonitrile at room temperature. Color: yellow (62%, M.p. 230–232 °C). Anal. Calcd. for C$_{28}$H$_{36}$N$_{12}$Cu$_2$O$_4$S$_4$Cl$_2$: C, 36.18; H, 4.39; N, 18.06 %. Found: C, 36.09; H, 3.87; N, 18.05%. IR (KBr, cm$^{-1}$, selected absorption bands): $\nu$(N$^1$–H) 3394br; $\nu$(N$^2$–H) 3121br; $\nu$(C–H) 3013m, 2989w, 2947m, 2878w; $\nu$(C=N) + $\nu$(C=C) 1588m, 1522m; $\nu$(C–N) 1092s, 1028s, 939m; $\nu$(C=S) 799s. $^1$H NMR (δ, ppm; CDCl$_3$): δ = 11.82 (2H, s, N$^2$H), 8.13 (2H, s, C$^2$H), 7.57 (2H, s, C$^6$H), 7.43 (2H, s, C$^4$H + CDCl$_3$), 6.79 (2H, s, C$^5$H), 6.52 (2H, db, N$^1$H), 3.23 (6H, d, CH$_3$) ppm.

[Cu$_2$Cl$_2$(μ-S-HttscN-Me)$_2$(κ$^1$-S-HttscN-Me)$_2$] (74)

To a light yellow solution of HttscN-Me (0.058 g, 0.293 mmol) in methanol (10 mL) was added CuCl$_2$ (0.025 g, 0.147 mmol) and the contents were stirred for 1 h. During stirring, dark green colored compound was separated, which was crystallized from a mixture of acetonitrile and methanol at room temperature. Color: pale olive-green (68%; M.p. 218–220 °C). Anal. Calcd. for C$_{28}$H$_{36}$N$_{12}$Cu$_2$S$_8$Cl$_2$: C, 33.70; H, 3.41; N, 16.85 %. Found: C, 33.76; H, 3.62; N, 16.88 %. IR (KBr, cm$^{-1}$, selected absorption bands): $\nu$(N$^1$–H) 3397br; $\nu$(N$^2$–H) 3113s; $\nu$(C–H) 3047m, 2997m, 2943br; $\nu$(C=N) + $\nu$(C=C) 1556s, 1529m; $\nu$(C–N) 1090s, 1028s, 932s; $\nu$(C=S) 802s. $^1$H NMR (δ, ppm; CDCl$_3$): δ = 11.78 (2H, s, N$_2$H), 8.39 (2H, s, C$_2$H), 7.57 (2H, s, C$_6$H), 7.43 (2H, s, C$_4$H), 7.29 (2H, s, C$_5$H + CDCl$_3$), 7.11 (2H, s, N$^1$H), 3.30 (6H, sb, CH$_3$) ppm.
To a solution of HbtscN-Me (0.054 g, 0.293 mmol) in methanol (10 mL) was added CuCl$_2$ (0.025 g, 0.147 mmol) and stirred for 2 h at room temperature. During stirring, white compound was separated, which was crystallized from a mixture of acetonitrile and methanol at room temperature. Color: colorless (68%, M.p. 225–227 °C). Anal. Calcd. for C$_{18}$H$_{22}$N$_6$CuS$_2$Cl: C, 44.71; H, 4.41; N, 17.39 %. Found: C, 44.49; H, 4.53; N, 17.30 %. IR (KBr, cm$^{-1}$, selected absorption bands): $\nu$(N–H) 3398br; $\nu$(N–H) 3115br; $\nu$(C–H) 3008m, 2958w, 2935m, 2889m; $\nu$(C=N) + $\nu$(C–C) 1554m, 1524m; $\nu$(C=S) 791s.

$^1$H NMR (ppm; CDCl$_3$): $\delta$ = 11.91 (2H, s, N$_2$H), 8.30 (2H, s, C$_2$H), 7.76 (4H, sb, C$_4$H + C$_8$H), 7.41 (6H, sb, C$_5$H + C$_6$H + C$_7$H), 7.32 (2H, s, N$_1$H + CDCl$_3$), 3.21 (6H, d, CH$_3$) ppm.

To a suspension of CoCl$_2$·6H$_2$O (0.025 g, 0.105 mmol) in toluene (10 mL) was added solid HttscN-Me (0.063 g, 0.315 mmol) and stirred for 2 h. Then contents were refluxed for 15 min. During refluxing black compound get separated along with Et$_3$NH$^+$Cl$^-$ salt. Both compounds were separated and crystals for X-ray were grown in CH$_2$Cl$_2$ and CH$_3$OH mixture (3:1 :: v/v). Color: black (71%, M.p. 150–152 °C). Anal. Calcd. for C$_{21}$H$_{26}$N$_9$CoOS$_6$: C, 37.51; H, 3.87; N, 18.76 %. Found: C, 37.89; H, 4.09; N, 18.68 %. IR (KBr, cm$^{-1}$, selected absorption bands): $\nu$(N–H) 3396s; $\nu$(C–H) 3048m, 2957m, 2929br; $\nu$(C=N) + $\nu$(C–C) 1510s, 1403s; $\nu$(C–N) 1045s; $\nu$(C=S) 767s. $^1$H NMR (δ, ppm; CDCl$_3$): δ = 7.56 (3H, d, C$_2$H), 7.40 (3H, m, C$_6$H), 7.23 (3H, m, C$_4$H), 7.05 (3H, m, C$_5$H), 5.22 (3H, sb, N$_1$H), 3.25 (9H, d, CH$_3$) ppm.
[Co(κ²-N₃,S-ftscN-Me)₃] (77)

It was prepared by a method similar to that for complex 76. Color: black (65%, M.p. 210–212 °C). Anal. Calcd. for C₂₁H₂₆N₉CoO₆S₆: C, 37.51; H, 3.87; N, 18.76 %. Found: C, 37.89; H, 4.09; N, 18.68 %. IR (KBr, cm⁻¹, selected absorption bands): ν(N–H) 3404br; ν(C–H) 3005w, 2959m, 2887w; ν(C=N) + ν(C–C) 1502s, 1402s; ν(C–N) 1084s, 1011s, 945m; ν(C–S) 750s. ¹H NMR (δ, ppm; CDCl₃): δ = 8.53 (3H, d, C₂H), 7.63 (3H, q, C₆H), 7.42 (3H, t, C⁴H), 6.59 (3H, t, C₅H), 5.25 (3H, sb, N¹H), 3.09 (9H, d, CH₃) ppm.

Chapter 5 describes spectroscopy, X-ray crystallography and other techniques, Chapter 6 gives analysis of results i.e., offers general comments on the formation of complexes, and Chapter 7 gives summary and conclusions of the work done.