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PAPER

Thiosemicarbazone derivatives of nickel and copper: the unprecedented coordination of furan ring in octahedral nickel(II) and of triphenylphosphine in three-coordinate copper(I) complexes†

Tarlok Singh Lobana,*[a] Poonam Kumari,[a] Rekha Sharma,[a] Alfonso Castineiras,[b] Ray Jay Butcher,[c] Takashiro Akitsu[d] and Yoshikazu Aritake[d]

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The influence of substituents at the C^2 carbon of N^1-substituted thiosemicarbazones, $\{C_4H_3X–C^2(CH_3)=N^3–N^2H–C^1(=S)N^1HR^2\}$ (X = O, S) on the geometry of nickel(II) complexes has been investigated. The presence of a methyl group at the C^2 position of 2-acetylfuran-N^1-substituted thiosemicarbazones $\{(C_4H_3O)–C^2(CH_3)=N^3–N^2H–C^1(=S)N^1HR^2$, $R^2 = CH_3$, HaftscN–Me; C_2H_5, HaftscN–Et; C_6H_5, HaftscN–Ph$\}$ induces unusual coordination by the furan ring and yielded high spin octahedral nickel(II) complexes, $[Ni(\kappa^3\text{-O}, N^3, \text{S-aftscN–R}^2)_2]$, CH_3 **1**, C_2H_5 **2**, and $2[Ni((\kappa^3\text{-O}, N^3, \text{S-aftscN–Ph})_2]$ **3** ($\mu_{eff} = 2.98$, **1**; 2.96, **2**; 2.92, **3**). With 2-acetylthiophene-N^1-substituted thiosemicarbazones, $\{(C_4H_3S)\text{-}C^2(CH_3)=N^3\text{-}N^2H–C^1(=S)N^1HR^2$, $R^2 = CH_3$, HattscN–Me; C_2H_5, HattscN–Et; C_6H_5, HattscN–Ph$\}$, N^3, S chelated low spin *trans* square planar complexes, $\{[Ni(\kappa^3\text{-O}, N^3, \text{S-attscN–R}^2)_2]$, $R^2 = CH_3$, **4**; C_2H_5, **5**; C_6H_5, **6**$\}$ with pendant thiophene rings have been obtained. The bigger sized sulfur atoms of the thiophene rings form short intramolecular contacts with the deprotonated hydrazinic nitrogen atoms ($S\cdots N^2$) inhibiting its lability for possible coordination to nickel(II). Complexes have one independent molecule (**1**) or two independent molecules (**2**, **3**) in their respective crystal lattices. The simultaneous presence of methyl groups at the C^2 and N^1 atoms of 2-acetylthiophene-N^1-methylthiosemicarbazone (HattscN–Me) have facilitated the binding of triphenylphosphine in three-coordinate copper(I) halide complexes, $[CuX(\eta^1\text{-S-HattscN–Me})(Ph_3P)]$ (X, Br, **7**; Cl, **8**), which represent an unusual donor set of ligands, namely, triphenylphosphine, sulfur of a thio-ligand and a halide.

Introduction

Coordination to metals by furan/thiophene through oxygen/sulfur donor atoms can be classified into three broad categories: as free, pendant or as a part of fused ring as depicted in Chart 1 (X = O, S). There is only one example in which free furan coordinates to a metal (namely, Cu) (type I),[1] and again one example in which it acts as an O, C- bridge (namely, Y) (type II).[2] Coordination by pendant furan (type III)[3–22] or fused furan rings (type IV)[23–32] make several examples. Most of the examples of coordination by pendant furan have been observed with alkali/alkaline and main group metals, and only a few with transition (Ti, Zr, Ag, Ru, Mo)/post transition (Cd, Lu, Sm, U) metals.[3–22] Similarly, free thiophene coordinates through sulfur (type I) or acts as a S, C- bridge (type II) (X = S) in several complexes,[33–40] and likewise coordination by pendant thiophene[6,38,41–54] or fused thiophene rings [26a,52c,55–62] is also widespread. In this case, complexes of ligands with pendant thiophene are essentially reported with transition (Cu, Ir, Mo, Pd, Re, Rh, Sc, Ag)/post transition metals (Hg).[41–54]

Surprisingly, there is no example of coordination of free or pendant furan/thiophene rings to nickel(II),[1–62] while in a few complexes, fused furan/thiophene has shown coordination to nickel(II).[25,55c,57] Also, there is no example of coordination by pendant furan or thiophene in complexes of thiosemicarbazones.[63] The impetus to carry out this investigation is primarily due to our experience in nickel(II)-furan/thiophene thiosemicarbazone chemistry.[64] It was observed that furan/thiophene rings remained pendant in *cis* or *trans* nickel(II) square planar complexes with N^1-substituted thiosemicarbazones (Chart 2, R^1 = H).[64] This made us

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[a] *Department of Chemistry, Guru Nanak Dev University, Amritsar, 143 005, India. E-mail: tarlokslobana@yahoo.co.in; Fax: +91-183-2-258820*
[b] *Departamento De Quimica Inorganica, Facultad de Farmacia, Universidad de Santiago, 15782, Santiago, Spain*
[c] *Department of Chemistry, Howard University, Washington DC, 20059, USA*
[d] *Department of Chemistry, Tokyo University of Science, Tokyo, 1628601, Japan*

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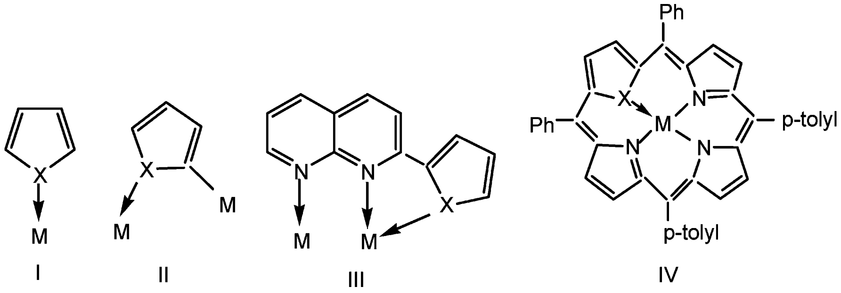
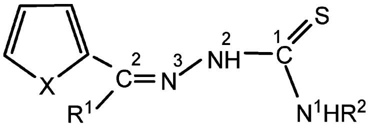


Chart 1 Coordination to metals by furan/thiophene (X = O, S).



$R^1 = CH_3$, X = O, S

X= O, $R^2 = CH_3$, 2-acetyl furan-N-methyl thiosemicarbazone (HaftscN-Me)
$R^2 = C_2H_5$, 2-acetyl furan-N-ethyl thiosemicarbazone (HaftscN-Et)
$R^2 = C_6H_5$, 2-acetyl furan-N-phenyl thiosemicarbazone (HaftscN-Ph)
X= S, $R^2 = CH_3$, 2-acetyl thiophene-N-methyl thiosemicarbazone (HattscN-Me)
$R^2 = C_2H_5$, 2-acetyl thiophene-N-ethyl thiosemicarbazone (HattscN-Et)
$R^2 = C_6H_5$, 2-acetyl thiophene-N-phenyl thiosemicarbazone (HattscN-Ph)

Chart 2 The different ligands used in this work.

curious to investigate coordination by pendant furan/thiophene rings to nickel(II) by changing substituents at the C^2 carbon as shown in Chart 2.

A series of ligands (R^1 = Me, R^2 = Me, Et, Ph) have been used for preparing complexes of nickel(II) in which effect of R^1 on the nature of the complexes is investigated. For R^1 = Me at C^2 and R^2 = Me at N^1, the reactions with copper(I) halides have also been investigated. The results of the investigations based on these ligands are herein reported.

Experimental Section

General. $Ni(OAc)_2{\cdot}4H_2O$, $CuSO_4{\cdot}5H_2O$, 2-acetylfuran-2-carbaldehyde, 2-acetylthiophene-2-carbaldehyde, N-methyl-, N-ethyl- and N-phenyl-thiosemicarbazides were procured from Sigma-Aldrich Ltd. The ligands HaftscN–Me, HaftscN–Et, HaftscN–Ph, HattscN–Me, HattscN–Et and HattscN–Ph were synthesized by conventional procedures.[65] Copper(I) halides were prepared by reducing an aqueous solution of $CuSO_4{\cdot}5H_2O$ using SO_2 in the presence of NaX (X = Cl, Br, I) in water.[66]

Synthesis of [Ni(aftscN–Me)$_2$] 1. To a light yellow solution of the HaftscN–Me ligand (0.039 g, 0.200 mmol) in methanol (15 mL) solid $Ni(OAc)_2$ (0.025 g, 0.100 mmol) was added. 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, a brown colored compound was separated, which was recrystallized in a dichloromethane and methanol mixture (3 : 1 v/v). Yield: 0.034 g, 75%. Anal. Calcd (%) for $C_{16}H_{20}N_6NiO_2S_2$: 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): 3367 br ($\nu(N^1–H)$); 3153 m, 2942 m, 2903 m ((C–H)); 1558 s, 1541 s (ν(C═N) + ν(C–C)); 1072 s, 1019 s, 913 s (ν(C–N)); 737 s (ν(C–S)). Electronic absorption spectrum (10^{-4} M in CH_3OH, λ_{max}/nm, ε/L mol^{-1} cm^{-1}): 982 (540), 671 (510), 406 (2.37×10^4), 331 (1.99×10^4), 301 (2.09×10^4), 247 (1.95×10^4). ^1H NMR (δ, $CDCl_3$ + DMSO-d_6): δ 31.86 (1H, s, C^6H), 19.58 (1H, s, C^4H), 17.64 (1H, s, C^5H), 6.76 (3H, s, $CH_3(C^2)$), 6.48 (3H, s, $CH_3(N^1)$), –4.09 (1H, s, N^1H) ppm. Magnetic moment: μ_{eff} = 2.98 BM.

Compounds **2–6** were prepared by a similar method.

Synthesis of [Ni(aftscN–Et)$_2$] 2. Yield: 0.037 g, 76%. Anal. Calcd. (%) for $C_{18}H_{24}N_6NiO_2S_2$: 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): 3372 br ($\nu(N^1–H)$); 3081 m, 2975 m, 2875 m (ν(C–H)); 1558 s, 1507 s (ν(C═N) + ν(C–C)); 1065 s, 1021 s, 916 s (ν(C–N)); 735 s (ν(C–S)). Electronic absorption spectrum (10^{-4} M in CH_3OH, λ_{max}/nm, ε/L mol^{-1} cm^{-1}): 983 (410), 675 (380), 405 (2.37×10^4), 331 (1.99×10^4), 301 (2.09×10^4), 248 (1.95×10^4).^1H NMR (δ, $CDCl_3$ + DMSO-d_6): δ 29.38 (1H, s, C^6H), 18.04 (1H, s, C^4H), 16.64 (1H, s, C^5H), 5.02 (5H, s, $CH_3(C^2)$ + $CH_2(N^1)$), 3.94 (3H, s, $CH_3(N^1)$), –3.01 (1H, s, N^1H) ppm. Magnetic moment: μ_{eff} = 2.96 BM.

Synthesis of [Ni(aftscN–Ph)$_2$] 3. Yield: 0.044 g, 77%. Anal. Calcd. (%) for $C_{26}H_{24}N_6NiO_2S_2$: 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): 3394 br ($\nu(N^1–H)$); 3103 m, 3023 m, 2950 m (ν(C–H)); 1554 s, 1520 s (ν(C═N) + ν(C–C)); 1085 s, 1023 m, 917 s (ν(C–N)); 731 s (ν(C–S)). Electronic absorption spectrum (10^{-4} M in CH_3OH, λ_{max}/nm, ε/L mol^{-1} cm^{-1}): 986 (390), 678 (350), 408 (2.39×10^4), 330 (1.98×10^4), 301 (2.09×10^4), 248 (1.94×10^4).

^{1}H NMR (δ, $CDCl_3$ + DMSO-d_6): δ 24.40 (1H, s, C^{6}H), 15.91 (1H, s, C^{4}H), 14.17 (1H, s, C^{5}H), 9.79 (2H, s, *o*-H(Ph)), 7.91 (3H, s, *p*-H+*m*-H(Ph)), 7.05 (3H, s, CH_3(C^2)), −1.12 (1H, s, N^{1}H) ppm. Magnetic moment: μ_{eff} = 2.92 BM.

Synthesis of [Ni(attscN–Me)$_2$] 4. Yield: 0.036 g, 74%, Anal. Calcd. (%) for $C_{16}H_{20}N_6NiS_4$: 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): 3395 br (ν(N–H)); 3056 m, 2905 m (ν(C–H)); 1558 s, 1507 s (ν(C═N) + ν(C═C)); 1069 s, 1025 m, 978 s (ν(C–N)); 713 s (ν(C–S)). Electronic absorption spectrum (10^{-4} M in CH_3OH, λ_{max}/nm, ε/L mol^{-1} cm^{-1}): 412 (0.40 × 10^4), 337 (1.28 × 10^4), 270 (1.10 × 10^4), 229 (1.09 × 10^4). ^{1}H NMR (δ, $CDCl_3$): δ 7.45 (1H, t, C^{6}H), 6.91 (1H, s, N^{1}H), 6.57 (1H, s, C^{4}H), 6.22 (1H, s, C^{5}H), 3.81 (3H, s, CH_3(C^2)), 1.56 (3H, s, CH_3(N^1) + DMSO) ppm.

Synthesis of [Ni(attscN–Et)$_2$] 5. Yield: 0.038 g, 74%. Anal. Calcd. (%) for $C_{18}H_{24}N_6NiS_4$: 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): 3357 br (ν(N^1–H)); 3093 m, 3056 m, 2987 m, 2871 (ν(C–H)); 1560 s, 1507 s (ν(C═N) + ν(C═C)); 1074 s, 1046 m, 1002 m (ν(C–N)); 737 s (ν(C–S)). Electronic absorption spectrum (10^{-4} M in CH_3OH, λ_{max}/nm, ε/L mol^{-1} cm^{-1}): 410 (0.40 × 10^4), 343 (1.41 × 10^4), 269 (1.26 × 10^4), 231 (1.18 × 10^4). ^{1}H NMR (δ, $CDCl_3$): δ 7.37 (1H, dd, C^{6}H), 6.71 (1H, d, C^{4}H), 6.47 (1H, d, C^{5}H), 6.10 (1H, s, N^{1}H), 4.24 (2H, s, CH_2), 2.20 (3H, s, CH_3(C^2) + DMSO), 1.26 (3H, s, CH_3(N^1)) ppm.

Synthesis of [Ni(attscN–Ph)$_2$] 6. Yield: 0.035 g, 58%. Anal. Calcd. (%) for $C_{26}H_{24}N_6NiS_4$: 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): 3408 m (ν(N^1–H)); 3088 m, 2930 m, 2857 m (ν(C–H)); 1558 s, 1507 s (ν(C═N) + ν(C═C)); 1050 s, 1025 m (ν(C–N)); 752 s (ν(C–S)). Electronic absorption spectrum (10^{-4} M in CH_3OH, λ_{max}/nm, ε/L mol^{-1} cm^{-1}): 415 (0.52 × 10^4), 343 (1.89 × 10^4), 264 (2.28 × 10^4), 213 (1.50 × 10^4). ^{1}H NMR (δ, $CDCl_3$): δ 8.88 (1H, d, N^{1}H) 7.46 (2H, m, *o*-H(Ph)), 7.37 (1H, d, C^{6}H), 7.30 (m, *p*-H(Ph) + $CDCl_3$), 7.14 (1H, t, C^{4}H), 7.04 (2H, m, *m*-H(Ph)), 6.92 (1H, q, C^{5}H), 2.80 (3H, s, (CH_3(C^2)) ppm.

Synthesis of [CuBr(HattscN–Me)(Ph$_3$P)] 7. To copper(I) bromide (0.025 g, 0.174 mmol) in 15 mL acetonitrile, the ligand HattscN–Me (0.037 g, 0.174 mmol) was added, and the contents stirred for 3–4 h. It formed yellow precipitates and addition of Ph_3P (0.046 g, 0.174 mmol) followed by stirring for 5–10 min formed a clear solution, which on slow evaporation at room temperature yielded yellow crystals. Yield: 0.063 g, 72%. Anal. Calcd. (%) for $C_{26}H_{26}CuBrN_3S_2P$: C, 50.44; H, 4.20; N, 6.79. Found: C, 50.57; H, 4.26; N, 6.73. IR (KBr, cm^{-1}, selected absorption bands): 3365 s ν(N^{1}H); 3129 m ν(N^{2}H); 2925 m, 2789 w, 2755 m ν(C–H); 1642 m, 1570 m ν(C═N) + ν(C═C); 1093 s ν(P–C$_{Ph}$); 1029 s ν(C–N); 801 s ν(C═S). ^{1}H NMR (δ, $CDCl_3$): 11.42 (1H, s, –N^{2}H), 7.31–7.57 (18H, m, C^{4,6}H + PPh_3 + N^{1}H), 7.02 (1H, dd, C^{5}H), 3.22 (3H, d, –CH_3(C^2)), 2.60 (3H, d, CH_3(N^1)) ppm. ^{31}P NMR (δ, $CDCl_3$): 31.2 ppm, $\Delta\delta$ ($\delta_{complex}$ − δ_{ligand}) 35. 8 ppm.

Complex **8** was prepared by a similar method.

Synthesis of [CuCl(HattscN–Me)(Ph$_3$P)] 8. Yield: 0.079 g, 67%. Anal. Calcd. (%) for $C_{26}H_{26}CuClN_3S_2P$: C, 54.35; H, 4.56; N, 7.31. Found: C, 54.17; H, 4.56; N, 7.22. IR (KBr, cm^{-1}, selected absorption bands): 3360 s ν(N^{1}H); 3119 m ν(N^{2}H); 2920 m, 2788 w, 2765 m ν(C–H); 1640 m, 1575 m ν(C═N) + ν(C═C); 1095 s ν(P–C$_{Ph}$); 1029 s ν(C–N); 795 s ν(C═S). ^{1}H NMR (δ, $CDCl_3$): 11.30 s (1H, s, N^{2}H), 7.35–7.53 (18H, m, C^{4,6}H + PPh_3 + N^{1}H), 7.01 (1H, dd, C^{5}H), 3.12 (3H, d, CH_3(C^2)), 2.56 (3H, d, CH_3(N^1)) ppm. ^{31}P NMR (δ, $CDCl_3$): 30.8 ppm, $\Delta\delta$ ($\delta_{complex}$ − δ_{ligand}) 35. 4 ppm.

Physical measurements. Elemental analyses for C, H and N were carried out using a thermoelectron FLASHEA1112 analyser. The melting points were determined with a Gallenkamp electrically heated apparatus. UV-visible spectra were recorded using a UV-1601PC Shimadzu spectrophotometer. Magnetic susceptibility was recorded using Magnetic Susceptibility balance procured from Johnson Matthey, Catalytic Systems Division Equipment. The IR spectra of the ligands and their complexes were recorded using KBr pellets in the range 4000–400 cm^{-1} on the FTIR-SHIMADZU 8400 Fourier Transform Spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL AL-300 FT spectrometer operating at a frequency of 300 MHz in $CDCl_3$ with TMS as the internal reference. ^{31}P NMR spectra were recorded at 121.5 MHz with $(CH_3O)_3P$ as the external reference taken as zero position.

X-ray crystallography. The single crystals of compounds were mounted on Bruker X8 KappaAPEXII (**1–5**) and CCD area detector (**7** and **8**) diffractometer, equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 100(2) K for **1–5**, and at 294(2) and 173(2) K for **7** and **8** respectively. The data were processed with APEX2[67a] (**1–5**), Bruker SMART[67b] (**7**, **8**) (data collection, cell refinement), Bruker SAINT[67b] (**7**, **8**) (data reduction) corrected for absorption using SADABS[67c] (**1–5**) (transmissions factors: 1.000–0.871). The structure was solved by direct methods using the program SHELXS-97[67d] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[67e] Compounds **2** and **5** present a chiral crystal structure. For **2** (space group $P2_1$) the structure was refined as a racemic twin with components 0.31(6) and 0.67(6) for the Flack parameter (absolute structure parameter), and for **5** (space group $C2$) the Flack parameter was calculated to be 0.03(2) for the present structure and 0.98(2) for the inverted structure. Criteria of a satisfactory complete analysis were the ratios of "rms" shift to standard deviation less than 0.001 and no significant features in the final difference maps. Atomic scattering factors from "International Tables for Crystallography".[67f] Molecular graphics from PLATON[67g] (**1–5**), Bruker SHELXTL[67h] (**7** and **8**). Table 1 contains crystal data for complexes **1–5**, **7** and **8**. Crystallographic data of ligand (HaftscN–Me) and bond distances and other data for complexes **1–5**, **7** and **8** are placed as supplementary information.†

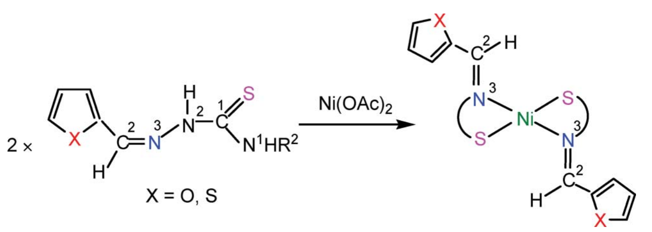
Results and discussion

(a) Nickel complexes

Synthesis and coordination by furan rings. Nickel(II) acetate with heterocyclic N^1-substituted thiosemicarbazones {C_4H_3X–C^2(R^1)═N^3–N^{2}H–C^1(═S)N^{1}HR^2, X = O, S} in methanol formed square planar complexes of stoichiometry, [NiL$_2$] (L = ftscN-R^2, ttscN-R^2), for R^1 as a hydrogen substituent at the C^2 carbon (Scheme 1).[64] Furan or thiophene rings remained pendant and

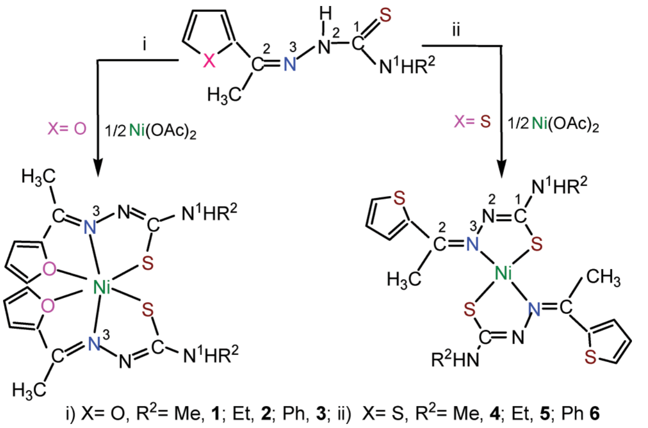
Table 1 Crystallographic data for complexes **1–5**, **7** and **8**

	1	**2**	**3**	**4**	**5**	**7**	**8**
Empirical formula	$C_{16}H_{20}N_6NiO_2S_2$	$C_{18}H_{24}N_6NiO_2S_2$	$C_{26}H_{24}N_6NiO_2S_2$	$C_{16}H_{20}N_6NiS_4$	$C_{18}H_{24}N_6NiS_4$	$C_{26}H_{26}BrCuN_3PS_2$	$C_{26}H_{24}ClCuN_3PS_2$
M	451.21	479.26	575.34	483.33	511.38	619.04	572.59
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	173(2)	294(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$Pna2_1$	$P2_1$	$C2/c$	$Aea2$	$C2$	$P\bar{1}$	$P\bar{1}$
a/Å	17.7919(7)	8.6756(10)	40.740(2)	14.768(2)	16.0268(9)	10.4662(11)	10.5576(11)
b/Å	8.5738(3)	14.1780(13)	18.3113(10)	27.394(3)	5.0807(4)	11.0814(12)	11.0223(12)
c/Å	12.8045(4)	17.316(2)	11.8250(7)	4.8820(6)	14.6896(11)	13.6967(15)	13.6843(14)
α (°)	90.00	90.00	90.00	90.00	90.00	70.189(2)	70.6420(10)
β (°)	90.00	93.068(8)	100.677(2)	90.00	113.493(3)	71.693(2)	72.3500(10)
γ (°)	90.00	90.00	90.00	90.00	90.00	63.524(2)	63.7540(10)
V/Å^3	1953.25(12)	2126.9(4)	8668.8(8)	1975.00(4)	1096.99(13)	1312.5(2)	1324.2(2)
Z	4	4	12	4	2	2	2
D_c/g cm^{-3}	1.534	1.497	1.323	1.625	1.548	1.566	1.436
μ/mm^{-1}	1.231	1.136	0.849	1.420	1.283	2.595	1.164
Reflections collected	84118	36267	92858	11660	8268	8007	7683
Independent reflections	4000 [R(int) = 0.0469]	8292 [R(int) = 0.1016]	8881 [R(int) = 0.0458]	1925 [R(int) = 0.0545]	1982 [R(int) = 0.0639]	5637 [R_{int} = 0.0329]	5896 [R_{int} = 0.0171]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0161, wR_2 = 0.0388	R_1 = 0.0312, wR_2 = 0.0912	R_1 = 0.0296, wR_2 = 0.0746	R_1 = 0.0261, wR_2 = 0.0802	R_1 = 0.0373, wR_2 = 0.0689	R_1 = 0.0398, wR_2 = 0.0939	R_1 = 0.0456, wR_2 = 0.1324



Scheme 1 Synthesis of complexes with R^1 = H substituent at the C^2 carbon.

did not show any coordination for different substituents at the N^1 nitrogen (R^2 = Me, Et, Ph). For R^1 as a methyl substituent at the C^2 carbon in place of hydrogen, a series of new complexes, namely, [NiL$_2$] {L = aftscN–R^2, R^2 = Me **1**, Et **2**, Ph **3**, attscN–R^2, R^2 = Me **4**, Et **5**, Ph **6**} have been isolated (Scheme 2).



Scheme 2 Synthesis of complexes with R^1 = CH$_3$ substituent at the C^2 carbon.

The IR and NMR spectral data of the complexes have shown disappearance of the hydrazinic protons (N^2–H) and it reveals that thio-ligands are coordinating as uninegative anions. The electron absorption spectral data (d-d transitions and charge transfer transitions)[68a] and μ values support octahedral geometry for the furan complexes and a square planar geometry for the thiophene complexes. The paramagnetism of complexes **1–3** revealed that the furan ring is probably coordinating to nickel(II) metal. A single crystal X-ray study (*vide infra*) later confirmed octahedral geometry for complexes with coordinated furan rings (**1–3**), and square planar for complexes with pendant thiophene rings (**4–6**) (Scheme 2).

Molecular structures. Molecular structures of complexes **1–3** are shown in Fig. 1–3 respectively. In these complexes, the uninegative thio-ligands are coordinated to the nickel metal center. The sulfur and furan ring oxygen atoms occupy *cis* positions of the octahedron and the azomethine nitrogen atoms occupy *trans* positions. The furan rings form short O–Ni–O bite angles in complexes, {73.26(4), 79.89(10), and 80.03(13)° respectively}, other angles surrounding nickel(II) suggest severely distorted octahedral geometry. Nickel–furan bond distances (Ni–O) lie in the range 2.202(3) –2.358(11) Å, which are close to the bond distances (2.093–2.120 Å) observed in the tetrakis(μ$_2$-(4-methoxyphenyl) dithiophosphonato- O, S, S′)-tetra-aquatetrakis(tetrahydrofuran)-tetra-nickel(II) complex[68b] and 2.184, 2.139 Å observed in nickel(II)

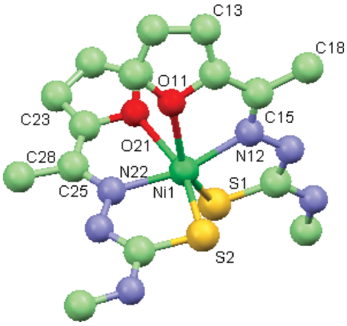


Fig. 1 Molecular structure of complex [Ni(aftscN–Me)$_2$] **1**.

complexes involving fused furan ring coordination.[25] An analysis of the X-ray structure of one of the furan ligands (HaftscN–Me, Fig. 4) revealed that H···H contact between the methyl hydrogen at the C^2 carbon (numbering is C^3 in ligand's structure, Fig. 4) and the furan ring hydrogen (C^4–H···H–C^6, 2.110 Å) is increased {C–H···H–C: 2.452, 2.486, 2.407 Å in complexes **1–3** respectively}. Complex **1** exists as a single molecule (Fig. 1) and complexes **2** and **3** exist as two independent molecules in their respective crystal lattices (Fig. 2 and 3).

Complexes **4–6** do not show coordination by the thiophene ring and have *trans* square planar geometries (Fig. 5). These complexes exist as single molecules in their respective crystal lattices, a behavior different from that of furan complexes. It is found that the bigger sized sulfur atoms of thiophene rings form short intramolecular contacts with the deprotonated hydrazinic nitrogen atoms (S···N^2) inhibiting its lability for possible coordination to nickel(II). These S···N^2 interactions in complexes **4** and **5** (2.63, 2.65 Å respectively) are much shorter than the sum of the van der Waals radius of S and N, 3.35 Å.[69]

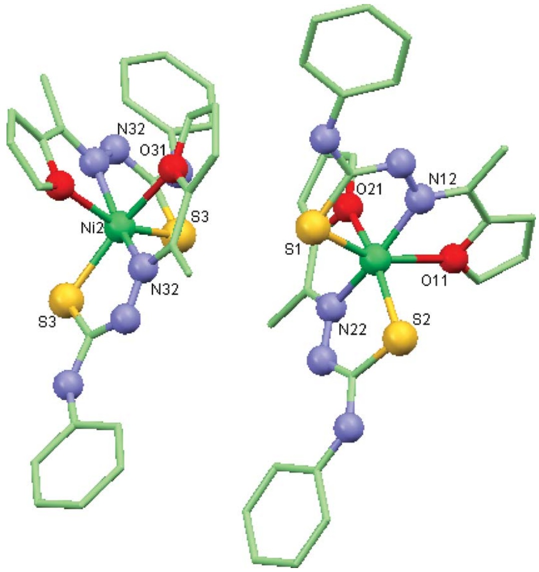


Fig. 3 Molecular structure of complex of [Ni(aftscN–Ph)$_2$] **3**.

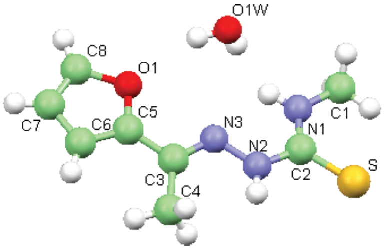


Fig. 4 Molecular structure of the ligand HaftscN–Me.

Packing interactions. An analysis of the packing diagrams of complexes **1–5** reveals interesting trends of inter- and intramolecular interactions which are influenced by the presence of the substituents at the C^2 and N^1 atoms of thiosemicarbazones. The sulfur atoms of thiophene rings are exhibiting short intramolecular contacts with the deprotonated hydrazinic (–N^2–) nitrogen atom which lowers the fluxional ability of the thiophene rings. The lack of a similar interaction (O···N^2) for the furan derivatives leads to a different pattern of bonding and intermolecular interactions.

In complex [Ni(aftscN–Me)$_2$] **1**, the deprotonated hydrazinic nitrogen atom (–N^2–) of one molecule interacts with hydrogen atom (at N^1) of the adjacent molecule {N^2···H–N^1, 2.33 Å}. This leads to the formation of a zig-zag 1D chain. Between these 1D chains there are (furan)C–H···N^2 (2.58 Å) and (furan)C–H···π(C=N^2) (2.85 Å) interactions, thus a 2D polymeric sheet

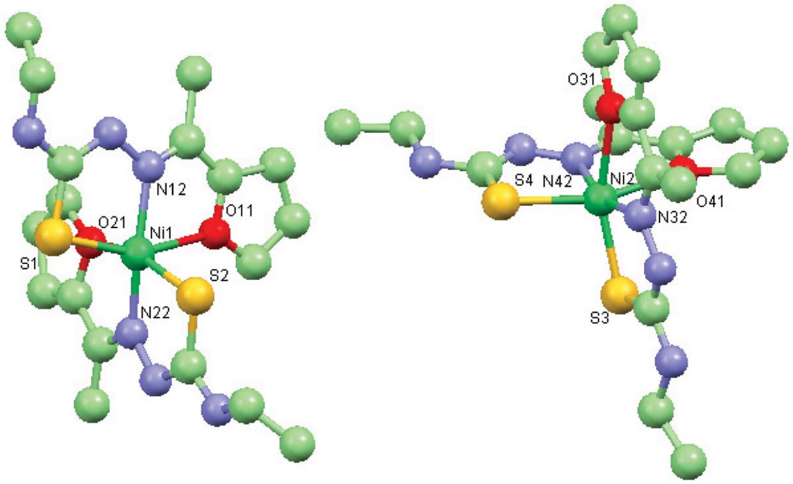


Fig. 2 Molecular structure of complex [Ni(aftscN–Et)$_2$] **2** showing the enantiomers A (Ni1) and B (Ni2) present in the asymmetric unit.

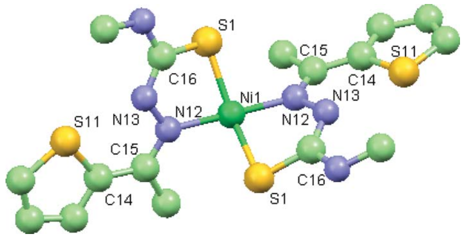


Fig. 5 Molecular structure of complex [Ni(attscN–Me)$_2$] **4** (complex **5** has a similar structure).

is formed (Fig. 6). In contrast in complex [Ni(aftscN–Et)$_2$] **2**, hydrogen at the N^1 nitrogen of one molecule interacts with the sulfur atom of the adjacent molecule {N^1–H$\cdots$S–C, 2.73 Å}. This interaction forms a 1D zig-zag chain. The interaction between chains {(furan)C–H$\cdots$N^1, 2.72 Å and (furan)C–H$\cdots\pi$(C=N^2), 2.81 Å} results in the formation of 2D sheet (see supplementary information†).

In complex [Ni(aftscN–Ph)$_2$] **3**, there are two independent molecules (Type I and Type II) in the crystal lattice. Type I molecules interact with one another through furan–phenyl {(furan)C–H$\cdots\pi$(phenyl), 3.004 Å) and amino–methyl {H–N$^1\cdots$H–CH$_2$(C^2), 2.618 Å} groups. Type II molecules interact with this arrangement from its top and bottom through C–S, CH$_3$ and phenyl moieties {C–S$\cdots$H–CH$_2$(C^2), 2.827, C–S$\cdots$H–C(furan), 2.957, (phenyl)C–H$\cdots\pi$(phenyl), 2.861 Å} as shown in Fig. 7. This unit of six molecules interacts with a similar unit *via* (phenyl)C–H$\cdots$N^2, 2.661 and C–S$\cdots$H–N^1, 2.660 Å (Fig. 8a). This unit of twelve molecules in the *ab* plane forms the basic core which interacts with similar units along the *c*-axis resulting in the formation of a 3D sheet.

In complex [Ni(attscN–Me)$_2$] **4**, a hydrogen atom (at N^1) of one molecule interacts with a sulfur atom of the adjacent molecule {C–S$\cdots$H–N^1, 2.73 Å} and this process continues to form a linear 1D chain. The chains then interact with one another through a second set of sulfur and hydrogen atoms (at N^1) resulting in the formation of a 2D sheet. In complex **5**, a 1D chain is similarly formed {C–S$\cdots$H–N^1, 2.82 Å **5**} and these chains link to one another through C$^2\cdots$H–CH–N^1 (2.85 Å), C–S$\cdots$H–CH$_2$CH$_2$–N^1 (2.83 Å) interactions and form a 2D sheet (see supplementary information†).

From above it is noted that the lack of a methyl substituent at C^2 resulted in square planar complexes with the furan or thiophene rings remaining pendant.[64] The presence of a methyl group at C^2 has induced coordination by the furan ring, but thiophene still remains pendant. It appears that weak Lewis basicity of the furan ring is enhanced by the inductive effect of the methyl substituent at the C^2 carbon. Further, there is an increase in electron density around the nickel center by N^3, S- chelation which appears to assist in the formation of nickel(II)–furan ring coordination. Stereochemically, it has been found that H$\cdots$H contact between the methyl hydrogen at the C^2 carbon and the furan ring hydrogen is increased in complexes **1–3**. Thus both the electronic and steric factors appear to be responsible for furan ring coordination. As regards the thiophene ring, it is found that the bigger sized sulfur atoms of thiophene rings form short intramolecular contacts with the deprotonated hydrazinic nitrogen atoms (S$\cdots$N^2) inhibiting its lability for possible coordination to nickel(II). The formation of Ni–O is also favored in terms of the HSAB principle over Ni–S bonds.

(b) Copper complexes

As an extension, the thiosemicarbazones under investigation were reacted with copper(II) salts, which however reduced Cu^{II} to Cu^{I}. This observation was in line with our previous reactions of thiosemicarbazones with copper(II) halides, wherein thiosemicarbazones, {C$_4$H$_3$X–C^2(H)=N^3–N^{2}H–C^1(=S)N^{1}HMe, X = O, S} reduced copper(II) halides to copper(I) halides and formed dinuclear copper(I) halide complexes, [Cu$_2$X$_2$(μ-S–L)$_2$(η^1-S–L)$_2$] in which furan or thiophene rings remained pendant.[70] Thus in this section reactions of 2-acetylthiophene-N^1-methyl thiosemicarbazone directly with copper(I) halides in the presence of Ph$_3$P have been carried out.

The reactions of 2-acetylthiophene-N^1-methyl thiosemicarbazones (R^1 = Me, R^2 = Me) with copper(I) halides in the presence of triphenylphosphine have formed complexes of stoichiometry {CuX(HattscN–Me)(Ph$_3$P)} (X = Br, Cl). The IR spectra confirmed the presence of characteristic ν(N–H), ν(C=S) and ν(P–C$_{\mathrm{Ph}}$) bands of HattscN–Me and Ph$_3$P ligands in complexes. The ^{1}H NMR spectra revealed the presence of N^{1}H, N^{2}H, methyl and phenyl signals and support the view that complexes have

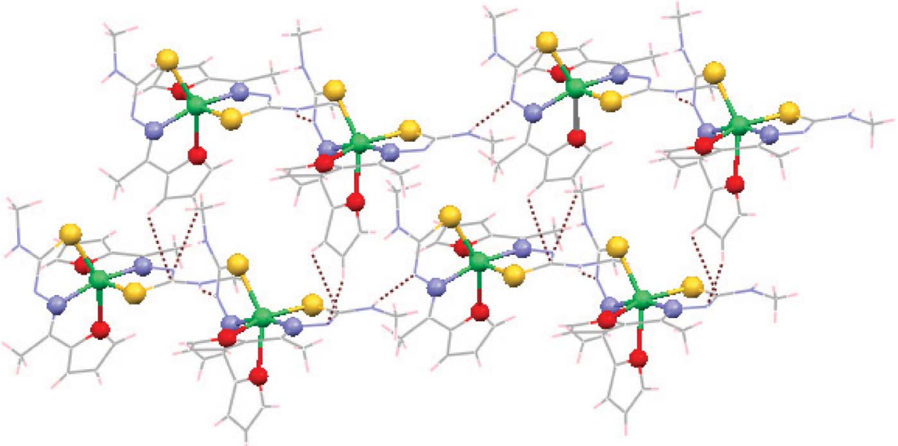


Fig. 6 Packing diagram of complex **1**, showing 2D network.

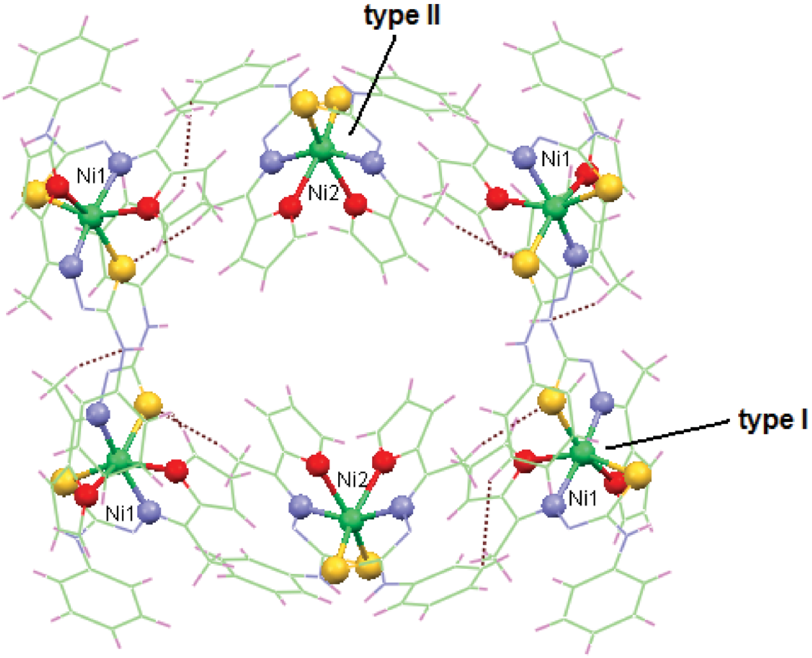


Fig. 7 Interactions of Type I and II molecules with one another.

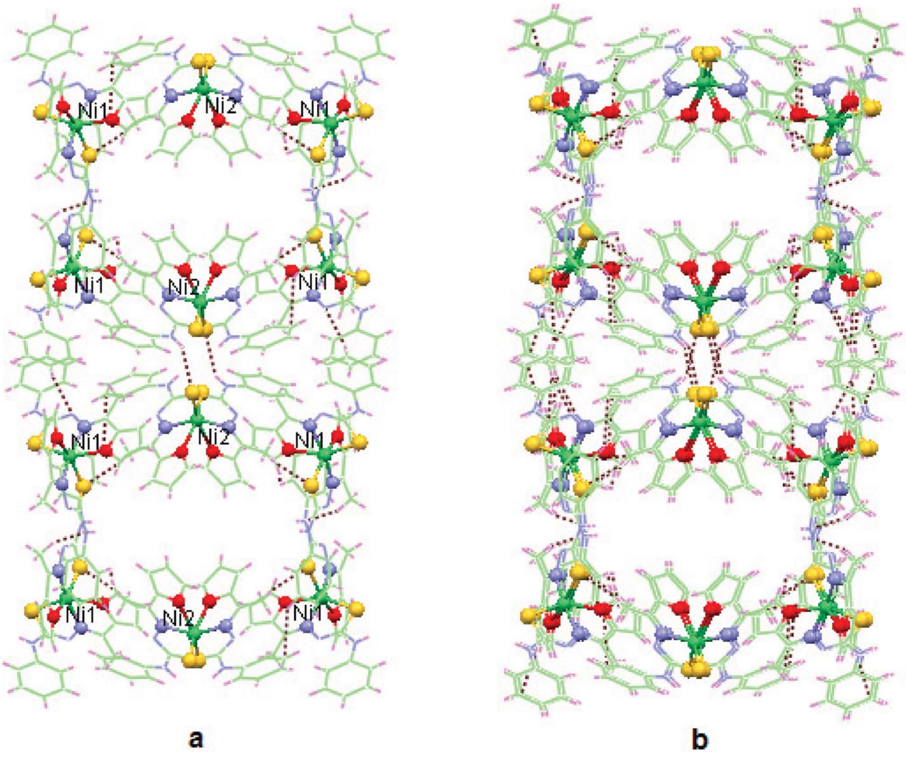
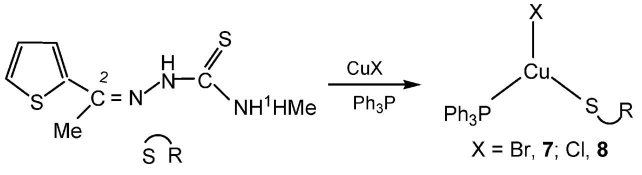


Fig. 8 Packing diagram of complex **3** showing a 2D (a) and 3D network (b).

neutral thio-ligands. A single crystal X-ray study has shown the formation of three-coordinate complexes, [CuX(η^1-S-HattscN–Me)(Ph_3P)] (X = Br **7**, Cl **8**) (Scheme 3). Recently, it has been demonstrated that the substituents at the C^2 and N^1 atoms of thiosemicarbazones influence the nuclearity and nature of bonding of metal complexes.[63,71–77] For example, in the case of thiophene thiosemicarbazones, a sulfur-bridged dimer (type A) was obtained when R^1 and R^2 were hydrogens (I, Chart 3).[73] With a methyl group at the C^2 carbon (R^1 = Me, R^2 = H), again a type A dimer was formed. Further, when hydrogen at the N^1 atom was replaced by a methyl group (R^1 = H, R^2 = Me), the sulfur-bridging changed to halogen-bridging (type B, Chart 3).[74] Interestingly, for



Scheme 3

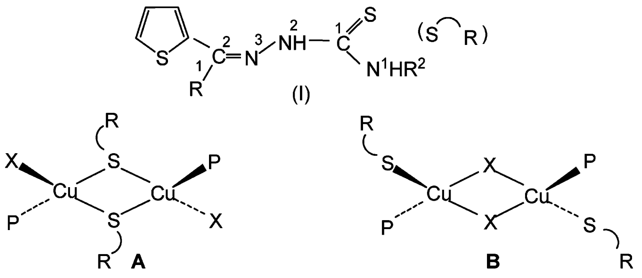


Chart 3 P = Ph$_3$P, X = Cl, Br, I.

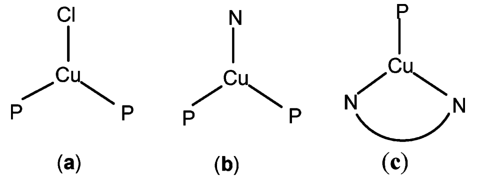


Chart 4 (a) P = (Ph)$_2$PC$_6$H$_4$CHO, (b) P = Ph$_3$P, N = (*p*-tolyl)$_2$N, (c) P = (cyhexl)$_3$P, N = 1, 10 phen.

R^1 and R^2 as methyl groups, neither a sulfur-bridged dimer **A** nor a halogen-bridged dimer **B** were formed as anticipated, rather three coordinate complexes were obtained. Therefore, the presence of methyl groups at both the C^2 and N^1 atoms of thiophene thiosemicarbazones (R^1 = R^2 = Me) has played an important role in stabilizing a coordination number of three with a new combination of ligands. It is reported that triphenylphosphine coordinates to copper(I) in a tetrahedral environment.[78–81]

Three coordinate copper(I) complexes with cores, [CuXP$_2$] (a),[82] [CuNP$_2$)] (b),[85] and [CuP(N–N)]BF$_4$ (c)[86] (Chart 4) have displayed interesting photophysical luminescence.[82–88] Here, in case (b), Ph$_3$P is bonded in a three coordinate environment with (*o*-tolyl)$_2$N$^-$ as the anion and cases (a) or (c), are exhibited by Ph$_2$PCH$_2$CHO and (cyhexl)$_2$P$^-$ respectively. Finally, tri-*o*-tolylphosphine formed three coordinate copper(I) complexes with heterocyclic thioamides.[83]

The geometry around copper(I) is distorted trigonal planar for complex **7**, {S–Cu–P, 125.98(4); S–Cu–Br, 122.37(3); P–Cu–Br, 111.53(3)°}, with usual copper–halogen, copper–sulfur and copper–phosphorous bond distances {Cu–Br, 2.3725(6); Cu–S, 2.2180(11); Cu–P, 2.2225(10) Å} (Fig. 9A).[63,69–71] Fig. 9B shows how three-coordinate molecules of complex **7** are interlinked in the crystal lattice. Two molecules are linked to one another through an intermolecular interaction between the hydrogen of a methyl group at the C^2 carbon and bromine, which form an H-bonded dimer. The H-bonded dimers are linked to one another through $\pi\cdots\pi$ interactions leading to the formation of a 1D chain. Complex **8** has a similar molecular structure and intermolecular interactions (see supplementary information†).

It is important to understand the interactions which may have assisted in the formation of three coordinate copper(I) complexes of triphenylphosphine. In complex **7**, there are intramolecular interactions involving amino hydrogen–imido nitrogen {CH$_3$N^{1}H$\cdots$N^3, 2.168 Å, 107.74°}, methyl hydrogen–sulfur {H$_2$CH$\cdots$S, 2.646 Å, 107.92°} and imino hydrogen–bromine atoms {N^{2}H$\cdots$Br, 2.587 Å, N–H$\cdots$Br, 153.60°} (Scheme 4). The bromine atom is also involved in intermolecular interactions. The methyl substituent at N^1 is engaged in H-bond formation with the coordinated sulfur {H$_2$CH$\cdots$S, 2.646 Å, C–H$\cdots$S, 107.92°}, and in a way blocking the possibility of dimerization through the sulfur donor atom. Likewise, the methyl substituent at the C^2 carbon is involved in an intermolecular interaction with the bromine atom {H$_2$CH$\cdots$Br, 2.847 Å, 162.84°}. The bromine is also H-bonded to hydrogen at the N^2 atom thus making it difficult for bromine to act as a bridge. All the intra- and inter-molecular interactions are strong as these distances are less than the sum of van der Waals radii {H, Br, 3.00–3.45; H, S, 3.00–3.45; H, N, 2.75–3.00 Å}.[69]

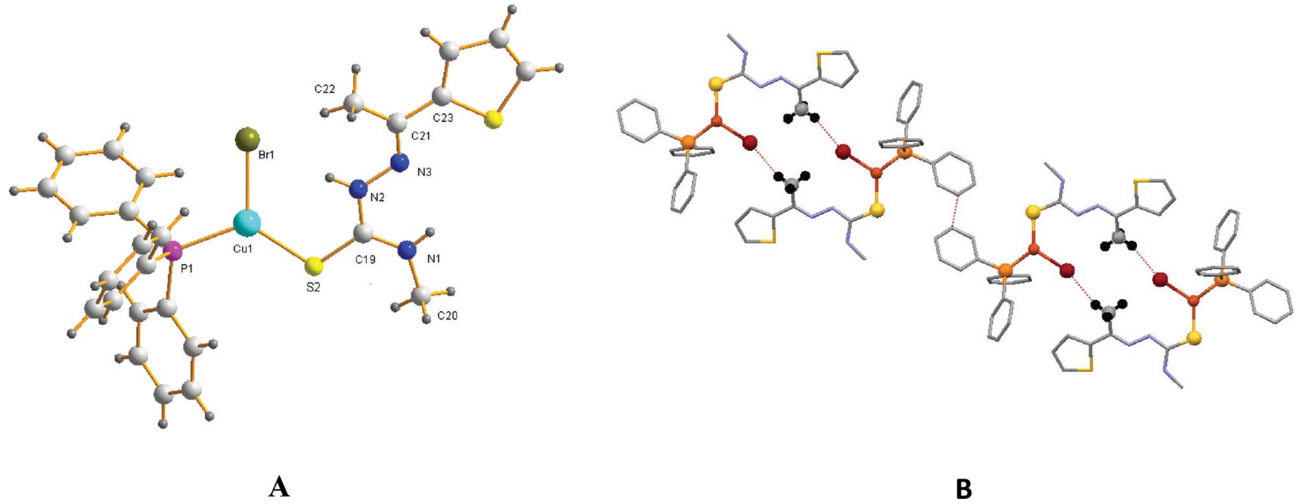
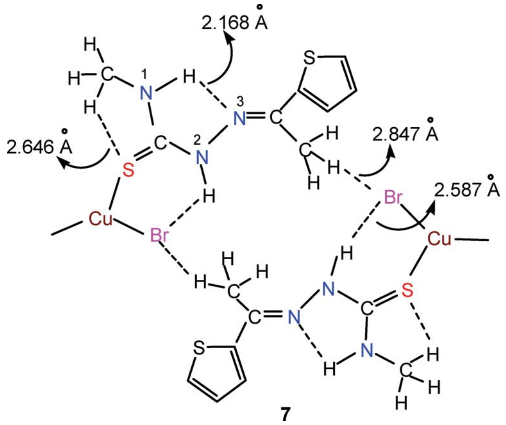


Fig. 9 Structure of complex **7** with atomic numbering scheme (A). Packing diagram of complex **7** showing a 1D chain (B).



Scheme 4 Various intra- and inter-molecular interactions of [CuBr(η^1-S-HattscMe)(Ph_3P)] **7**.

Conclusions

In this investigation, two different five membered heterocyclic rings at the C^2 carbon of N^1-substituted thiosemicarbazone ligands, $\{C_4H_3X–C^2(R^1){=}N^3–N^2H–C^1({=}S)N^1HR^2$, X = O, S; R^2 = Me, Et, Ph$\}$ have shown different behavior in their interaction with nickel(II) acetate. For R^1 = Me at the C^2 carbon in place of H (R^2 = Me, Et, Ph), furan ring coordination has been observed resulting in the formation of octahedral complexes. However, for R^1 = Me at C^2, the thiophene ring remained pendant and formed N^3, S- chelated square planar complexes. The formation of a tunnel in complex **3** is unprecedented (phenyl substituent at the N^1 nitrogen). The methyl groups at the C^2 and N^1 atoms of 2-acetylthiophene-N^1-methyl thiosemicarbazone favor three-coordinate complexes in which copper(I) is bonded to a thio-ligand, a halogen and triphenylphosphine.

Acknowledgements

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