Supplementary

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

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Spectroscopy (IR, NMR, UV-vis)

The ligands show IR bands due to $\nu$(N1-H) and $\nu$(N2-H) moieties in the region, 3459–3206 cm$^{-1}$. In their respective complexes 1–8, bands due to $\nu$(N1-H) appears in the the range, 3408–3357 cm$^{-1}$. The $\nu$(N2-H) bands appear at 3129 and 3119 cm$^{-1}$ in complexes 7 and 8 while this band disappear in complexes 1–6. This reveals that the ligands are coordinated to the metal center in the anionic form in complexes 1–6 and in neutral form in complexes 7 and 8. The diagnostic $\nu$(C-S) bands lie in the range, 713–752 cm$^{-1}$ in the complexes 1–6 and $\nu$(C=S) band at 848 and 795 cm$^{-1}$ in complexes 7 and 8 respectively (cf. free ligands, 819–739 cm$^{-1}$). Other characteristic bands are given in the experimental section.

Free ligands (HaftsN-R$^2$, HattsN-R$^2$; R$^2$= Me, Et, Ph) show a signal at low field (8.56–9.40 ppm) due to the presence of hydrazinic proton (-N2H-). This signal appears at $\delta$ 11.42 and 11.30 ppm in complexes 7 and 8 respectively, which shows a downfield shift vis-à-vis free ligands which confirmed that thio- ligands are coordinating to Cu in neutral form. Further, the $^{31}$P NMR spectra of complexes 7 and 8 showed one signal at $\delta$ 31.2 and 30.8 ppm respectively, with a coordination shift of $\Delta$δ 35.8 (7) and 35.4 (8) ppm. However this signal is absent in the spectra of complexes 3–6, thus confirming
deprotonation of these ligands in their respective complexes. Complexes 1–3 are paramagnetic, so their NMR spectra were recorded by opening the window from +100 to -100 ppm. In these complexes, signals show downfield shift relative to their respective ligands, except N1H signal (-4.09, 1; -3.01, 2; -1.12 ppm, 3). In complexes 4–8, signals are well resolved and are given in the experimental section.

In the O, N, S- donor ligand, HaftscN-Me, the intense absorption bands at 207, 220 and 314 nm are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. These bands in complex 1 appear at 247 and 301 nm. Two bands at 331 and 406 nm are assigned to S$\rightarrow$Ni charge transfer transitions, while the bands at 671 and 982 nm are assigned to the d-d transitions: $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ respectively. The various transitions in complexes 2 and 3 are assigned as follows: $\pi \rightarrow \pi^*$ (248, 2; 247, 3), $n \rightarrow \pi^*$ (301, 1; 301, 3), S$\rightarrow$Ni(CT) (331, 405, 2; 330, 408 3), $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ (675, 2; 681, 3) and $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ (983, 2; 985, 3) (Table 1). Similarly, in the N, S- donor ligand, HattscN-Me, the $\pi \rightarrow \pi^*$ (213, 257 nm) shift to 229 nm in square planar complex 4. The $n \rightarrow \pi^*$ transition (320 nm in ligand) merges with LMCT (S$\rightarrow$Ni) + $\nu_3$(d-d) transitions and appears as an intense band at 337 nm. A band at 412 nm, attributed to $^1A_{1g} \rightarrow ^1A_{2g}$ transition, appears as shoulder to main band. Complexes 5 and 6, have shown similar transitions in the ranges: 212–269 ($\pi \rightarrow \pi^*$), 343 (n$\rightarrow\pi^*$, S$\rightarrow$Ni + $^1A_{1g} \rightarrow ^1E_g$) and 410–415 nm ($^1A_{1g} \rightarrow ^1A_{2g}$) (Table 2).

**IR spectra of the ligands**

**HaftscN-Me**: IR (KBr, cm$^{-1}$, selected absorption bands): 3445br ($\nu$(N1-H)); 3241s ($\nu$(N2-H)); 3051w, 2984w ($\nu$(C-H)); 1555s, 1496s ($\nu$(C=N) + $\nu$(C=C)); 1077s, 1047s ($\nu$(C-N)); 739s ($\nu$(C-S)).

**HaftscN-Et**: IR (KBr, cm$^{-1}$, selected absorption bands): 3334br ($\nu$(N1-H)); 3272br ($\nu$(N2-H)); 2977w, 2940w, 2866w ($\nu$(C-H)); 1539s, 1517s ($\nu$(C=N) + $\nu$(C=C)); $\nu$(C-N)); 744s ($\nu$(C-S)).

**HaftscN-Ph**: IR (KBr, cm$^{-1}$, selected absorption bands): 3459s ($\nu$(N1-H)); 3341s ($\nu$(N2-H)); 3155w, 3103w, 2835w ($\nu$(C-H)); 1558s, 1526s ($\nu$(C=N) + $\nu$(C=C)); 1068s, 1018s, 934s ($\nu$(C-N)); 757s ($\nu$(C-S)).
HattscN-Me: IR (KBr, cm\(^{-1}\), selected absorption bands): 3446br (\(\nu(N^1-H)\)); 3385s (\(\nu(N^2-H)\)); 2989w, 2931w (\(\nu(C-H)\)); 1558s, 1542s (\(\nu(C=N) + \nu(C=C)\)); 1053s, 1035s, 959s (\(\nu(C-N)\)); 819s (\(\nu(C-S)\)).

HattscN-Et: IR (KBr, cm\(^{-1}\), selected absorption bands): 3358br (\(\nu(N^1-H)\)); 3206s (\(\nu(N^2-H)\)); 3128w, 2962w, 2882w (\(\nu(C-H)\)); 1596s, 1517s (\(\nu(C=N) + \nu(C=C)\)); 1096s, 1053s, 967s (\(\nu(C-N)\)); 811s (\(\nu(C-S)\)).

HattscN-Ph: IR (KBr, cm\(^{-1}\), selected absorption bands): 3390br (\(\nu(N^1-H)\)); 3248s (\(\nu(N^2-H)\)); 3052w, 2906w (\(\nu(C-H)\)); 1587s, 1531s (\(\nu(C=N) + \nu(C=C)\)); 1047s, 1027s (\(\nu(C-N)\)); 817s (\(\nu(C-S)\)).

1\(^{H}\) NMR spectra of ligands: HattscN-Me, \(^{1}\)H NMR (\(\delta\), CDCl\(_3\)): \(\delta\) 8.62 (1H, s, \(N^2\)H), 7.66 (1H, s, br, \(N^1\)H), 7.48 (1H, dd, \(C^6\)H), 6.73 (1H, dd, \(C^4\)H), 6.47 (1H, q, \(C^5\)H), 3.25 (3H, t, \(CH_3(C^2)\)), 2.21 (3H, d, \(CH_3(N^1)\)) ppm. HattscN-Et, \(^{1}\)H NMR (\(\delta\), CDCl\(_3\)): \(\delta\) 8.56 (1H, s, \(N^2\)H), 7.66 (1H, s, br, \(N^1\)H), 7.59 (1H, d, \(C^6\)H), 6.72 (1H, s, \(C^4\)H), 6.47 (1H, dd, \(C^5\)H), 3.72 (2H, m, CH2), 2.20 (3H, d, \(CH_3(C^2)\)), 1.69 (s, 3H, \(CH_3(N^1)\)) ppm. HattscN-Ph, \(^{1}\)H NMR (\(\delta\), CDCl\(_3\)): \(\delta\) 9.40 (1H, s, \(N^2\)H), 8.71 (1H, s, \(N^1\)H), 7.69 (2H, m, \(o-H(Ph)\)), 7.52 (1H, dd, \(p-H(Ph)\)), 7.40 (1H, m, \(m-H(Ph)\)), 7.24 (2H, dd, \(C^6\)H), 6.79 (1H, dd, \(C^4\)H), 6.54 (1H, dd, \(C^5\)H), 2.35 (3H, s, \(CH_3(C^2)\)) ppm. HattscN-Me, \(^{1}\)H NMR (\(\delta\), CDCl\(_3\)): \(\delta\) 8.59 (1H, s, \(N^2\)H), 7.52 (1H, s, br, \(N^1\)H), 7.34 (1H, dd, \(C^6\)H), 7.29 (1H, dd, \(C^4\)H), 7.03 (1H, q, \(C^5\)H), 3.27 (3H, t, \(CH_3(C^2)\)), 2.28 (3H, d, \(CH_3(N^1)\)) ppm. HattscN-Et, \(^{1}\)H NMR (\(\delta\), CDCl\(_3\)): \(\delta\) 8.56 (1H, s, \(N^2\)H), 7.47 (1H, s, br, \(N^1\)H), 7.33 (1H, dd, \(C^6\)H), 7.29 (1H, m, \(C^4\)H), 7.03 (1H, m, \(C^5\)H), 3.76 (2H, m, CH2), 2.25 (3H, d, \(CH_3(C^2)\)), 1.34 (3H, s, \(CH_3(N^1)\)) ppm. HattscN-Ph, \(^{1}\)H NMR (\(\delta\), CDCl\(_3\)): \(\delta\) 9.30 (1H, s, \(N^2\)H), 8.69 (1H, s, \(N^1\)H), 7.71 (1H, d, \(C^6\)H), 7.69 ((1H, d, \(C^4\)H), 7.39 (3H, m, \(o-H+ \ p-H(Ph)\)), 7.23 (1H, t, \(m-H(Ph)\)), 7.06 (1H, q, \(C^5\)H), 2.31 (3H, d, \(CH_3(C^2)\)) ppm.
Table 1. Electronic spectral data: \(\lambda_{\text{max}}/\text{nm} \quad (\varepsilon / \text{L mol}^{-1} \text{ cm}^{-1}) \) a

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<th>Compound</th>
<th>(\pi \rightarrow \pi^*)</th>
<th>(n \rightarrow \pi^*)</th>
<th>LMCT(S(\rightarrow)Ni)</th>
<th>d-d</th>
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<td>301(20980)</td>
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<td>985(400)</td>
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a 10^{-4}\text{M in CH}_{3}\text{OH}

HafscN-Mea: 207(7080), 220 (4500) \(\pi \rightarrow \pi^*\), 314(18540) \(n \rightarrow \pi^*\)

HafscN-Eta: 208(7310), 233 (4340) \(\pi \rightarrow \pi^*\), 314(18100) \(n \rightarrow \pi^*\)

HafscN-Pha: 209(11140), 240 (7500) \(\pi \rightarrow \pi^*\), 320(18570) \(n \rightarrow \pi^*\)

Table 2. Electronic spectral data: \(\lambda_{\text{max}}/\text{nm} \quad (\varepsilon / \text{L mol}^{-1} \text{ cm}^{-1}) \) a

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<th>(\nu_2) (d-d)</th>
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<td>343(14080)</td>
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a 10^{-4}\text{M in CH}_{3}\text{OH},

HattscN-Mea: 213(12050), 257(10020) sh \(\pi \rightarrow \pi^*\), 320(24530) \(n \rightarrow \pi^*\)

HattscN-Eta: 212(3990), 260 sh(3590) \(\pi \rightarrow \pi^*\), 328(8990) \(n \rightarrow \pi^*\)

HattscN-Phb: 268 sh (8210) \(\pi \rightarrow \pi^*\), 336(8210) \(n \rightarrow \pi^*\)

b 10^{-4}\text{M in DMSO}

Crystal structure

Fig. 1 Molecular structure of complex [Ni(attsN-Et)$_2$] 5

Packing Interactions

Fig. 2 Packing diagram of complex 1, showing interaction, {N$_2^\ldots$H(N$^1$), 2.33 Å} in 1D chain
Fig. 3 Packing diagram of complex 2, showing interaction, {C-S···H(N¹), 2.73 Å} in 1D chain

Fig. 4 Packing diagram of complex 2, showing 2D network
Fig. 5 Packing interactions in 3, showing intermolecular interactions of type 1 molecules, \{C-S···HN\textsuperscript{1}, 2.734, (furan)C-H···(ph), 2.837, (furan)···(furan) 3.318 Å\} in 1D chain

Fig. 6 Packing diagram of complex 4, showing intramolecular, \{CaH\textsubscript{2}S···N\textsuperscript{2}, 2.63 Å\} and intermolecular interactions, \{C-S···HN\textsuperscript{1}, 2.73 Å\} in 1D chain
Fig. 7 Packing diagram of complex 4 showing 2D network

Fig. 8 Packing diagram of complex 5, showing intramolecular, \{C_4H_3S\cdots N^2, 2.65 \text{ Å}\} and intermolecular interactions, \{C-S\cdots HN^1, 2.82 \text{ Å}\} in 1D chain

Fig. 9 Packing diagram of complex 5, showing 2D network
Fig. 10 Molecular structure of complex [CuCl(η¹-S-HattscN-Me)(Ph₃P)]

Fig. 11 Packing diagram of complex 8

Scheme 1. Various intra- and inter-molecular interactions of [CuCl(η¹-S-HattscN-Me)(Ph₃P)]

Table 3. (C^2 methyl)C-H···H-C(furan) interactions in ligand (Haftsc-N-Me) according to our Chem. Draw Schemes are given below according to their X-ray structures of complexes (1–3)

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<th>C-H···H-C (Å)</th>
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<td>1</td>
<td>2.110 (C^4-H···H-C^6)</td>
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<tr>
<td>2</td>
<td>2.513 (C^28-H···H-C^23), 2.390 (C^18-H···H-C^13)</td>
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<tr>
<td>3</td>
<td>2.538 (C^20-H···H-C^14), 2.457 (C^30-H···H-C^24), 2.559 (C^40-H···H-C^34), 2.391 (C^50-H···H-C^44)</td>
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<td>4</td>
<td>2.342 (C^150-H···H-C^13), 2.430 (C^250-H···H-C^23), 2.450 (C^350-H···H-C^33)</td>
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Table 4. Hydrogen Bonds (Å)

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<th>C-S···H-N1</th>
<th>(furan)C-H···N1</th>
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Table 5. Selected bond lengths (Å) and bond angles (°) of complexes 1–5, 7 and 8

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**Complex 2**

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**Second independent molecule**

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**Complex 3**

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**Second independent molecule**

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The single crystal of compound (HaftscN-Me) was mounted on Xcalibur, Ruby, Gemini diffractometer, equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 123(2) K.
Table 6. Crystallographic data of ligand HaftscN-Me

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