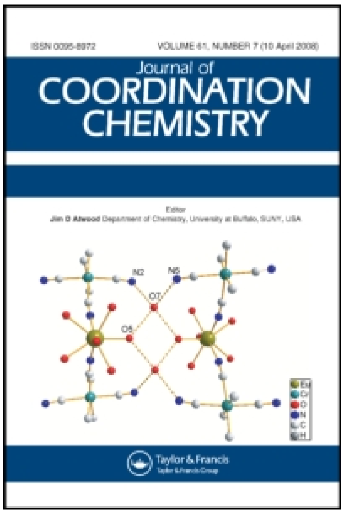

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Unusual template condensation of benzophenone thiosemicarbazones and salicylaldehydes with nickel(II)

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Unusual template condensation of benzophenone thiosemicarbazones and salicylaldehydes with nickel(II)

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Reactions of 5-R-2-hydroxybenzophenone *S*-methylthiosemicarbazones (R: H, Br, Cl) and 2-hydroxy-benzaldehydes in the presence of $NiCl_2$ yielded template complexes by chelating with two of the ligands in the monoanionic form. The N_4O_2 complexes of the thiosemicarbazones show distorted-octahedral geometry around nickel(II). The compounds were characterized by elemental analysis, conductivity and magnetic measurements, UV-Vis, IR, ^{1}H-NMR, and mass spectra. Crystal structure of bis-N^1-(2-hydroxy-5-bromo-phenyl)(phenyl)methylene-N^4-(2-hydroxy-phenyl)methylene-S-methyl-thiosemicarbazidato-Ni(II) was determined by single-crystal X-ray diffraction.

Keywords: Thiosemicarbazone; Benzophenone; Template condensation; N_4O_2 complex; X-ray crystal structure

1. Introduction

Thiosemicarbazones and their metal complexes have a variety of biological activities ranging from antitumor, anticonvulsant, antifungal, antibacterial, antimicrobial, and antiviral activities [1–3]. Thiosemicarbazones are also used in the determination of trace metals in biological and pharmaceutical samples [4]. Because of these properties, transition metal complexes of thiosemicarbazone derivatives have been intensively studied in view of their structural chemistry and biological potential.

Thiosemicarbazones can be mono-, bi-, or tridentate ligands coordinating the metal through sulfur, azomethine nitrogen, and heteroatom of the condensed aldehyde or ketone [5–7]; bis-thiosemicarbazone derivatives can be tetradentate [4, 8]. Some tetradentate thiosemicarbazones have been synthesized by metal-directed condensation of thiosemicarbazones with carbonyl compounds. The template reaction of S-alkylthiosemicarbazones involve condensation of the thioamide (N^4H_2) of S-alkylthiosemicarbazone and carbonyl of an aldehyde or ketone in the presence of metal ion; the template complexes can have N_4, N_3O, or N_2O_2 binding systems [9–11]. To synthesize N_2O_2-type template complexes, Fe(III) [12, 13], Co(II) [14, 15],

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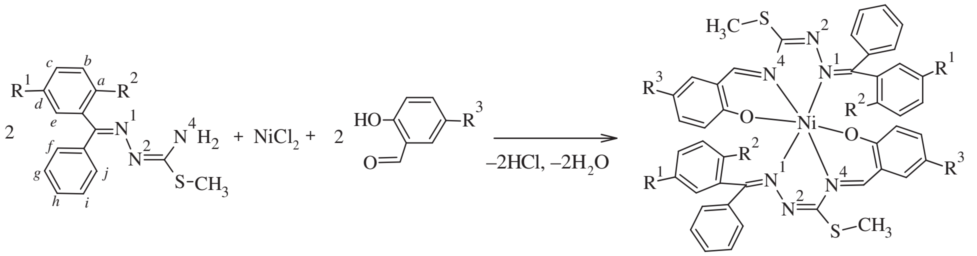

Figure 1. Template reaction scheme. Thiosemicarbazones, R^1/R^2: H/H (**L1**); Br/OH (**L2**); Cl/OH (**L3**), and complexes, $R^1/R^2/R^3$: H/H/H (**1**); H/H/Br (**2**); Br/OH/H (**3**); Br/OH/Br (**4**); Cl/OH/H (**5**); and Cl/OH/Br (**6**).

Ni(II) [16, 17], Cu(II) [18, 19], Zn [20, 21], Pd(II) [22], UO_2(II) [23], and VO(II) [24, 25] were used.

Herein, we report the first N_4O_2-type template complexes of nickel(II) in octahedral geometry synthesized by chelating with two monoanionic benzophenone thiosemicarbazones having ONN donor sets and 2-hydroxy-benzaldehydes. The ligands and 1 : 2 template compounds (figure 1) were characterized by elemental analysis, conductivity and magnetic measurements, UV-Vis, IR, ^{1}H-NMR, and mass spectra. The crystal structure of **3** was determined by single-crystal X-ray diffraction.

2. Experimental

2.1. *Chemicals and apparatus*

All chemicals were reagent grade and used as purchased. Analytical data were obtained with a Thermo Finnigan Flash EA 1112 analyzer and Unicam Solar 929 atomic absorption spectrometer. IR spectra of the compounds were recorded on KBr pellets with a Mattson 1000 FT-IR spectrometer. UV-Vis spectra were performed on an ATI-Unicam UV-Vis spectrometer UV2 Series. ^{1}H-NMR spectra were recorded on a Varian UNITY INOVA-500 MHz spectrometer relative to $SiMe_4$ using deuterated DMSO-d_6 as solvent. The APCI-MS analyses were carried out in positive and negative ion modes using a Thermo Finnigan LCQ Advantage MAX LC/MS/MS. Molar conductivities were measured using a digital CMD 750 conductivity meter. Magnetic measurements were carried out at room temperature by the Gouy technique with an MK I model device obtained from Sherwood Scientific.

2.2. *Crystallographic analyses*

A red, platelet crystal of $C_{44}H_{34}Br_2N_6NiO_4S_2$ having dimensions 0.40 × 0.20 × 0.10 mm was mounted on a glass fiber. The diffraction data was collected on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo-Kα (0.7107 Å) radiation at 294 K. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.63 to 1.00. The molecular and crystal structures were solved by direct methods using SIR92 [26, 27]. Hydrogens were refined using the riding model and non-hydrogen atoms were refined anisotropically. All calculations were performed using the Crystal Structure crystallographic software package [28, 29].

2.3. *Synthesis of benzophenone thiosemicarbazones*

The *S*-methylthiosemicarbazones, **L1**, **L2**, and **L3**, were prepared with small modifications of general methods [30, 31].

Benzophenone *S*-methylthiosemicarbazone (**L1**): benzophenone thiosemicarbazone (0.76 g, 3 mmol) was dissolved in THF (8 mL) at 60°C on a water bath. To the solution, methyl iodide (0.23 mL, 3.6 mmol) was added and the mixture was allowed to stand at room temperature for 24 h. The precipitated hydroiodide salt was filtered off and washed with cold diethyl ether (5 mL). The colorless product was dissolved in 5 mL alcohol by heating and neutralized with a sufficient amount of aqueous $NaHCO_3$ solution (10%, w/w). The precipitate was collected by filtration and washed with 10 mL portions of water and diethylether, respectively. The final product was recrystallized from ethanol. Yield 0.48 g (60%).

L2 and **L3** were synthesized by a similar procedure. The analytical, physical, UV-Vis [λ_{max}, nm (log ϵ), in DMF], FT-IR (KBr, cm^{-1}), ^{1}H-NMR (DMSO-d_6, 500 MHz, 25°C, δ ppm), and (+c APCI)-MS (m/z, %) data of the ligands were given as follows.

L1: yield 0.48 g (60%), m.p. 134.5°C. Anal. Calcd for $C_{15}H_{15}N_3S$ (%): C, 66.88; H, 5.61; N, 15.60; S, 11.90. Found (%): C, 66.75; H, 5.52; N, 15.49; S, 11.83. UV-Vis: 240 (4.38), 309 (4.39). FT-IR: $\nu(NH_2)$ 3472, 3287, $\delta(NH_2)$ 1639, $\nu(C{=}N^1)$ 1602, $\nu(N^2{=}C)$ 1589. ^{1}H-NMR: 7.63 (dd, 1H, *e*), 7.46–7.30 (m, 7H, *c–j*), 7.24 (dd, 1H, *b*), 7.18 (dd, 1H, *a*), 6.88, 6.64 (*cis*/*trans* ratio: 3/2, s, 2H, N*H₂*), 2.31, 2.08 (*cis*/*trans* ratio: 2/3, s, 3H, S-C*H₃*). MS m/z (%): $[M]^+$, 270.09 (100); $[M+H]^+$, 271.11 (18.77); $[M+2H]^+$, 272.10 (5.07); $[M-(-N{=}C(SCH_3)-NH_2)]^+$, 180.19 (4.74).

L2: yield 0.58 g (75%), m.p. 137°C. Anal. Calcd for $C_{15}H_{14}BrN_3OS$ (%): C, 49.46; H, 3.87; N, 11.54; S, 8.80. Found (%): C, 49.38; H, 3.94; N, 11.48; S, 8.71. UV-Vis: 242 (4.34), 306 (4.26). IR: $\nu(OH)$ 3312, $\nu(NH_2)$ 3466, 3442, $\delta(NH_2)$ 1634, $\nu(C{=}N^1)$ 1601, $\nu(N^2{=}C)$ 1592. ^{1}H-NMR: 10.28, 9.93 (*cis*/*trans* ratio: 2/1, s, 1H, 2-O*H*), 7.63 (dd, 1H, *e*), 7.47–7.30 (m, 5H, *f–j*), 7.00 (s, 2H, N*H₂*), 7.03 (dd, 1H, *c*), 6.87 (t, 1H, *b*), 2.34, 2.21 (*cis*/*trans* ratio: 3/2, s, 3H, S-CH_3). MS m/z (%): $[M]^+$, 364.01 (99.09); $[M+H]^+$, 365.05 (18.66); $[M+2H]^+$, 365.98 (100); $[M-(-N{=}C(SCH_3)-NH_2)]^+$, 274.17 (1.41).

L3: yield 0.53 g (55%), m.p. 169°C. Anal. Calcd for $C_{15}H_{14}ClN_3OS$ (%): C, 56.33; H, 4.41; N, 13.14; S, 10.03. Found (%): C, 56.26; H, 4.26; N, 12.94; S, 9.82. UV-Vis: 242 (4.47), 306 (4.45). IR: $\nu(OH)$ 3317, $\nu(NH_2)$ 3463, 3441, $\delta(NH_2)$ 1635, $\nu(C{=}N^1)$ 1604, $\nu(N^2{=}C)$ 1594. ^{1}H-NMR: 10.26, 9.91 (*cis*/*trans* ratio: 2/1, s, 1H, 2-O*H*), 7.63 (dd, 1H, *e*), 7.45-7.28 (m, 5H, *f–j*), 7.00 (s, 2H, N*H₂*), 6.93 (d, 1H, *c*), 6.90 (t, 1H, *b*), 2.34, 2.21 (*cis*/*trans* ratio: 3/2, s, 3H, S-CH_3). MS m/z (%): $[M]^+$, 320.06 (100); $[M+H]^+$, 321.08 (18.32); $[M+2H]^+$, 322.05 (38.72); $[M-(-N{=}C(SCH_3)-NH_2)]^+$, 230.23 (1.20).

2.4. *Synthesis of complexes*

Complex **1**: $NiCl_2\cdot6H_2O$ (0.24 g, 1 mmol) was dissolved in absolute ethanol (10 mL) and then 1.5 mL of ortho-formic ester was added to the solution. The solution was allowed to stand at room temperature for 24 h, after which a mixture of **L1** (0.27 g, 1 mmol) and salicylaldehyde (0.11 mL, 1 mmol) in absolute ethanol (10 mL) was added dropwise. The reaction mixture was stirred vigorously for 1 h, and then the solvent was reduced to half of its volume under vacuum. After standing at room temperature for 1 week, the resulting blackish-green precipitates were filtered off, washed with a mixture of ethanol/ether (1 : 1, 10 mL), and dried *in vacuo* over P_2O_5. Yield: 0.20 g (25%).

The nickel(II) templates (**2**–**6**) were prepared by the same synthesis. The colors, yield (%), m.p. (°C), μ_{eff} value (BM), molar conductivity ($ohm^{-1}\,cm^2\,mol^{-1}$, in 10^{-3} M DMF), elemental analysis and spectroscopic data of the complexes were given as follows.

Compound **1**: Blackish-green, 25, 251, 2.87, 0.04. Anal. Calcd for $C_{44}H_{36}N_6NiO_2S_2$ (%): C, 65.76; H, 4.52; N, 10.46; S, 7.98; Ni, 7.30. Found (%): C, 65.61; H, 4.52; N, 10.32; S, 7.78; Ni, 7.21. UV-Vis: 241 (4.77), 313 (4.51), 355 (4.56), 488 (4.36), 762 (2.78). IR: $\nu(C{=}N^1, N^2{=}C, N^4{=}C)$ 1616, 1585, 1555. MS *m*/*z* (%): $[M]^+$, 803.81 (61.40); $[M-H]^+$, 802.80 (100); $[M+H]^+$, 804.82 (59.66); $[M+2]^+$, 805.71 (24.30); $[M{-}(CH_3SH_2)]^+$, 754.65 (10.07); $\{M{-}[HOC_6H_4CH{=}N{-}C(SCH_3){=}N{-}N{=}C(C_6H_5)_2]\}^+$, 430.08 (26.85), $\{M{-}[HOC_6H_4{-}CH{=}N{-}C(SCH_3){=}N{-}N{=}C(C_6H_5)_2] + Ni\}^+$, 373.90 (16.89).

Compound **2**: Dark red, 15, 249, 3.07, 0.01. Anal. Calcd for $C_{44}H_{34}Br_2N_6NiO_2S_2$ (%): C, 54.97; H, 3.56; N, 8.74; S, 6.67; Ni, 6.10. Found (%): C, 54.81; H, 3.61; N, 8.64; S, 6.53; Ni, 6.16. UV-Vis: 239 (5.12), 307 (4.89), 355 (4.91), 498 (4.78), 762 (2.84). IR: $\nu(C{=}N^1, N^2{=}C, N^4{=}C)$ 1612, 1582, 1564. MS *m*/*z* (%): $[M]^+$, 961.66 (52.97); $[M-H]^+$, 960.63 (100); $[M+H]^+$, 962.63 (76.04); $[M+2H]^+$, 963.62 (34.74); $[M{-}(CH_3SH_2)]^+$, 912.64 (2.06); $\{M{-}[BrC_6H_3(O){-}CH{=}N{-}C(SCH_3){=}N{-}N{=}C(C_6H_5)_2]\}^+$, 510.09 (47.31); $\{M{-}[BrC_6H_3(O){-}CH{=}N{-}C(SCH_3){=}N{-}N{=}C(C_6H_5)_2] + Ni\}^+$, 451.99 (30.77).

Compound **3**: Brick red, 42, 254, 2.86, 0.01. Anal. Calcd for $C_{44}H_{34}Br_2N_6NiO_4S_2$ (%): C, 53.20; H, 3.45; N, 8.46; S, 6.46; Ni, 5.91. Found (%): C, 53.09; H, 3.38; N, 8.23; S, 6.34; Ni, 5.75. UV-Vis: 241 (5.09), 312 (4.83), 330 (4.84), 466 (4.60), 762 (3.07). IR: $\nu(OH)$ 3435, $\nu(C{=}N^1, N^2{=}C, N^4{=}C)$ 1609, 1578, 1559. MS *m*/*z* (%): $[M]^+$, 993.72 (13.41); $[M-H]^+$, 992.70 (22.85); $[M+H]^+$, 994.63 (19.81); $[M{-}(CH_3SH_2)]^+$, 946.62 (9.02); $\{M{-}[{-}OC_6H_4{-}CH{=}N{-}C(SCH_3){=}N{-}N{=}C(C_6H_5)(HOC_6H_3Br)]\}^+$, 526.11 (31.98); $\{M{-}[HOC_6H_4{-}CH{=}N{-}C(SCH_3){=}N{-}N{=}C(C_6H_5)(HOC_6H_3Br)] + Ni + H^+\}^+$, 470.00 (100).

Compound **4**: Brick red, 17, >350, 2.93, 0.01. Anal. Calcd for $C_{44}H_{32}Br_4N_6NiO_4S_2$ (%): C, 45.91; H, 2.80; N, 7.30; S, 5.57; Ni, 5.10. Found (%): C, 45.74; H, 2.70; N, 7.13; S, 5.46; Ni, 5.03. UV-Vis: 241 (5.01), 308 (4.67), 334 (4.68), 480 (4.48), 762 (2.85). IR: $\nu(OH)$ 3435, $\nu(C{=}N^1, N^2{=}C, N^4{=}C)$ 1610, 1583, 1557. MS *m*/*z* (%): $[M]^+$, 1151.44 (15.81); $[M-H]^+$, 1150.45 (29.04); $[M+H]^+$, 1152.38 (25.64); $[M{-}(CH_3SH_2)]^+$, 1102.39 (2.04); $\{M{-}[HOC_6H_3(Br){-}CH{=}N{-}C(SCH_3){=}N{-}N{=}C(C_6H_5)(HOC_6H_3Br)]\}^+$, 603.96 (40.62); $\{M{-}[HOC_6H_3(Br){-}CH{=}N{-}C(SCH_3){=}N{-}N{=}C(C_6H_5)(HOC_6H_3Br)]{+}Ni + H^+\}^+$, 547.90 (100).

Compound **5**: Brick red, 35, 258.5, 2.83, 0.02. Anal. Calcd for $C_{44}H_{34}Cl_2N_6NiO_4S_2$ (%): C, 58.43; H, 3.79; N, 9.29; S, 7.09; Ni, 6.49. Found (%): C, 58.32; H, 3.63; N, 9.11; S, 6.90; Ni, 6.39. UV-Vis: 242 (5.02), 311 (4.78), 333 (4.80), 468 (4.57), 763 (2.78). IR: $\nu(OH)$ 3441, $\nu(C{=}N^1, N^2{=}C, N^4{=}C)$ 1616, 1578, 1558. MS *m*/*z* (%): $[M]^+$, 904.75 (100);

$[M-H]^+$, 903.80 (45.74); $[M-2H]^+$, 902.76 (84.24); $[M+H]^+$, 905.76 (50.51); $[M+2H]^+$, 906.73 (50.88); $[M-(CH_3SH_2)]^+$, 854.86 (2.14); $\{M-[HOC_6H_4-CH=N-C(SCH_3)=N-N=C(C_6H_5)(HOC_6H_3Cl)]\}^+$, 480.11 (59.76); $\{M-[-OC_6H_4-CH=N-C(SCH_3)=N-N=C(C_6H_5)(HOC_6H_3Cl)]+Ni\}^+$, 423.25 (46.61).

Compound **6**: Bright black, 25, 307, 2.95, 0.01. Anal. Calcd for $C_{44}H_{32}Br_2Cl_2N_6NiO_4S_2$ (%): C, 49.75; H, 3.04; N, 7.91; S, 6.04; Ni, 5.53. Found (%): C, 49.72; H, 2.98; N, 7.82; S, 5.87; Ni, 5.46. UV-Vis: 240 (4.90), 308 (4.62), 331 (4.63), 480 (4.43), 762 (2.81). IR: ν(OH) 3426, ν($C=N^1$, $N^2=C$, $N^4=C$) 1608, 1582, 1562. MS m/z (%): $[M]^+$, 1062.42 (100); $[M-1]^+$, 1061.41 (42.81); $[M+1]^+$, 1063.43 (53.51); $[M-(CH_3SH_2)]^+$, 1013.37 (4.75); $\{M-[HOC_6H_3(Br)-CH=N-C(SCH_3)=N-N=C(C_6H_5)(HOC_6H_3Cl]\}^+$, 501.94 (67.50); $\{M-[-OC_6H_3(Br)-CH=N-C(SCH_3)=N(C_6H_5)(HOC_6H_3Cl)]+Ni\}^+$, 560.32 (72.24).

3. Results and discussion

3.1. *Physical properties*

5-(H/Br/Cl)-2-hydroxybenzophenone *S*-methylthiosemicarbazones are in the form of powder crystals and soluble in methanol, ethanol, and chlorinated hydrocarbons. Metal-directed condensation of the thiosemicarbazones with aldehydes gave stable compounds in a few minutes, but crystals of the products were obtained from the mother liquor after 1 week at room temperature.

The thiosemicarbazones, **L1**, **L2**, and **L3**, gave asymmetrical 1 : 2 template complexes through N_2O donor sets of two thiosemicarbazones in the monoanionic form even when a 1 : 1 : 1 mole ratio of the reactants (L1-3, $NiCl_2$, and aldehydes) was used (figure 1).

Template complexes (**1**–**6**) form as very fine crystal materials, very soluble in common organic solvents. The low molar conductances of the complexes indicate non-ionic structures. All of the complexes are stable in air and the magnetic susceptibility values (2.83–3.07 BM) are compatible with high-spin d^8 nickel(II) in an octahedral environment.

3.2. *Spectroscopic data*

The electronic absorption bands of the thiosemicarbazones and complexes were obtained in 3×10^{-5} M DMF solution between 200 and 800 nm. The spectra of the thiosemicarbazones revealed bands at 240 and 309 nm for **L1** and at 242 and 306 nm for **L2** and **L3**, which can be assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions associated with the thiosemicarbazone moiety and aromatic ring. In spectra of the nickel complexes, $\pi\rightarrow\pi^*$ transitions of the aromatic rings were recorded at 239–242 nm and $n\rightarrow\pi^*$ transitions of the azomethine and thioamide groups were observed at 307–313 nm and 330–355 nm region, respectively [32]. The spectra have two spin-allowed transitions predicted for an octahedral nickel(II) complex. The bands at 466–498 and 762–763 nm can be attributed to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ transitions [33, 34].

IR spectra of the thiosemicarbazones displayed typical OH, N^4H_2, $C=N^1$, $N^2=C$ vibrations and the expected proton signals in the NMR spectra also confirmed the structures of **L1**, **L2**, and **L3** [35, 36].

The template reaction of *S*-methylthiosemicarbazones with aldehydes can be easily monitored by IR spectra. The $\nu(N^4H_2)$ bands of **L1**, **L2**, **L3**, and ν(OH) band of the condensed aldehydes are absent in the complex spectra due to coordination of aldehyde hydroxyl by losing proton and the formation of a new C=N band between thioamide and the aldehyde. The $\nu(C{=}N^1)$ bands of **1**–**6** shifted to lower energies *ca* 19–27 cm^{-1} compared with free ligands, while $\nu(N^2{=}C)$ bands shifted *ca* 4–16 cm^{-1}. Medium-intensity bands of new azomethine groups, $(N^4{=}C)$, arising by condensation of the thioamide nitrogen and aldehyde, are observed at 1555–1564 cm^{-1}.

Mass specta of the ligands contain $[M-(-N{=}C(SCH_3)-NH_2)]^+$. All the complex spectra show peaks attributable to $[M-CH_3SH_2]^+$, $[M-L]^+$, and $[M-NiL]^+$. The M^+ and MH^+ fragments indicate expected molecular weight proving compositions $[Ni(L)_2]$.

3.3. *Crystal structure of 3*

Single crystals of **3** suitable for X-ray diffraction were grown by slow evaporation from a mixed solution of ethanol and chloroform (2 : 1, v/v) at room temperature. It crystallizes in a monoclinic crystal system with space group *P2₁/c* (#14). The relevant details of the crystal, data collection and structure refinement are found in table 1. Selected bond distances and angles are presented in tables 2 and 3. The complete list of bond distances, bond angles, atomic coordinates and anisotropic thermal parameters are presented in supporting information.

The six-coordinate nickel(II) (figure 2) bonds to two ligands, two nitrogens from thiosemicarbazone moiety, and one oxygen from salicyl in the NNO mode, forming N_4O_2 donor-set around nickel. The structure includes two five-membered NiN2C2 and two six-membered NiONC3 chelate rings.

The molecular geometry of the complex is distorted octahedron with asymmetric thiosemicarbazone. The N6–Ni1–N3 with 173.0(3)° angle can be designated as the *z* axis.

Table 1. Crystallographic data and processing parameters for **3**.

Empirical formula	$C_{44}H_{34}N_6O_4S_2NiBr_2$
Formula weight	993.42
Temperature (K)	294
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dimensions (Å, °)	
a	19.4005(3)
b	9.7276(2)
c	24.1438(4)
α	90
β	90.8241(11)
γ	90
Volume (Å^3), *Z*	4556.0(1), 4
Calculated density (g cm^{-3})	1.448
Absorption coefficient (Mo-Kα) (cm^{-1})	23.24
F(000)	2008.00
Limiting indices	$h=23$; $k=11$; $l_{max}=28$
Reflections collected	176,302
Independent reflection	8248 [R(int) = 0.095]
Observed reflection	7478
Goodness-of-fit on F^2	1.157
Final *R* indices [$I > 3\sigma(I)$], R_w [$I > 3\sigma(I)$]	$R_1=0.1455$, $wR_2=0.1600$

The other axes in the horizontal plane, O1–Ni1–N2 and O2–Ni1–N4, are bent with 162.5(3)° and 167.0(3)° angles. Lengths of coordination bonds are not equal and so the five-membered NiN2C2 and six-membered NiONC3 chelate rings are bent (table 2).

In crystal form, the molecular conformation of **3** is stabilized by C–X ··· Y (where X: Br, H, and O; Y: O and H), type intermolecular interactions. Four of them, H32 ··· O3,

Table 2. Coordination bond lengths and angles of **3**.

Bond lengths (Å)		Angles (°)			
Ni1–O1	2.071(6)	N6–Ni1–N3	173.0(3)	N6–Ni1–N4	77.7(3)
Ni1–N2	2.203(9)	O1–Ni1–N2	162.5(3)	N2–Ni1–N3	76.7(3)
Ni1–N4	2.216(7)	O2–Ni1–N4	167.0(3)	O1–Ni1–N3	86.9(3)
Ni1–O2	2.130(7)	O1–Ni1–N6	87.5(3)	O2–Ni1–N6	89.3(3)
Ni1–N6	2.038(9)	O2–Ni1–N3	95.3(3)	O1–Ni1–O2	94.8(3)
Ni1–N3	1.991(6)			N2–Ni1–N4	103.4(3)

Table 3. Interaction parameters related to oxygen (Å and °) in **3**.

C–X ··· O	d(D–X)	d(X ··· O)	d(D ··· O)	∠(DXO)
C5–H15 ··· O1^{i}	0.95	2.578	3.486	159.74
C5–H15 ··· O2^{i}	0.95	2.653	3.307	126.35
C38–H32 ··· O3^{ii}	0.95	2.608	3.301	129.98
C6–O3 ··· O2^{i}	1.356	2.263	3.326	107.21
C37–O2 ··· O3^{ii}	1.276	2.263	3.407	115.19

^{i}x, 1+y, z.
^{ii}x, −1+y, z.

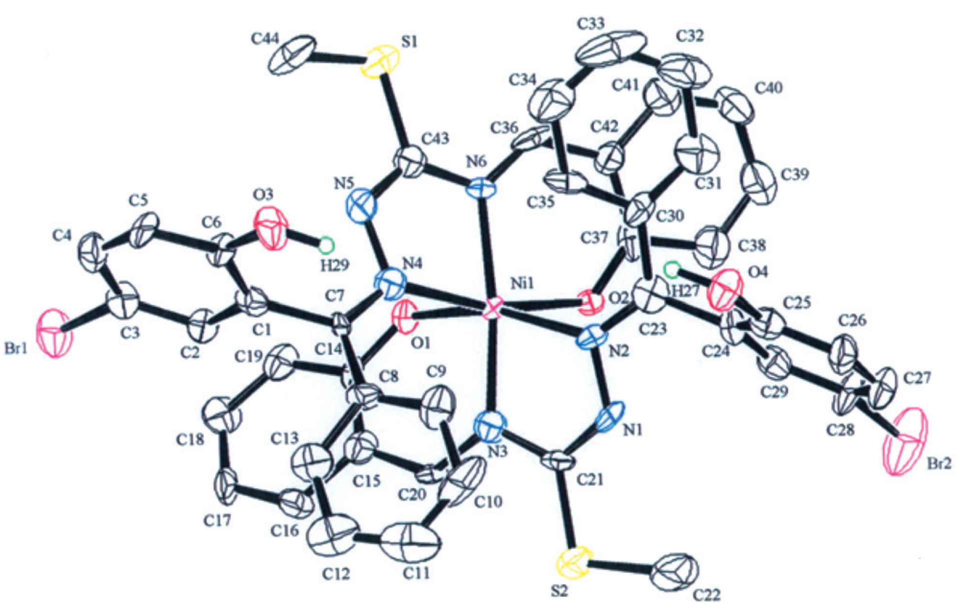

Figure 2. Molecular structure and atom-numbering scheme for **3**. The H atoms (except H27 and H29) have been omitted for clarity.

H15 ⋯ O1, H15 ⋯ O2, and O3 ⋯ O2, connect two molecules giving zig zag bonding (table 3). Propagation of this interaction motif generates a molecular chain and this chain structure repeats through other short contacts in the form of a parallel chain arrangement. Contacts with distances less than 3 Å are H5–Br1 2.988, H26–C17 2.857, H30–C25 2.890, H2–C38 2.727, H13–H31 2.157, and C14–H15 2.897.

4. Conclusion

The tendency of nickel(II) to form a square-planar complex has been reported for many common complexes of thiosemicarbazones and their template compounds [1, 4, 5, 37, 38]. In our previous study, 4-substituted 2-hydroxybenzophenone thiosemicarbazone gave expected square-planar complexes in N_2O_2 coordination mode [39].

In this study, the phenyl ring of the benzophenone thiosemicarbazone **L1** has no 2-OH substituent and can generate a tridentate donor set (N_2O). To complete the coordination sites of nickel(II), two tridentate ligands coordinate (**1** and **2**). In contrast, the 5-(Br/Cl)-2-hydroxy benzophenone thiosemicarbazones, **L2** and **L3**, gave tetradentate (N_2O_2) ligand systems and an octahedral structure involving N_4O_2 donors formed instead of the expected square-planar structure.

This unusual half-template condensation occurs by using the 5-substituted benzophenone thiosemicarbazone. 5-Bromo- and chloro-substituted phenol rings with relatively high acidity compared to 4-substituted phenol, and the hydroxyl protons of **L2** and **L3** are more dissociated. So, the deprotonated 2-OH of the benzophenone thiosemicarbazone cannot react with $NiCl_2$ and the template condensation is completed over only hydroxyl group of salicylaldehyde as second arylidene moiety.

The nickel in the template condensation of **L1**, **L2**, and **L3** showed a tendency to compose the maximum number of chelate rings due to the symbiosis effect and the coordination sites of nickel are occupied by N_2O donor set of two monoanionic thiosemicarbazones.

Supplementary material

Crystallographic data for [Ni(L)$_2$] ($C_{44}H_{34}Br_2N_6NiO_4S_2$ (**3**)) has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication (CCDC 711558). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk].

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