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ORIGINAL ARTICLE

Synthesis, characterization and structural studies of binuclear nickel(II) complexes derived from dihydroxybenzaldehyde thiosemicarbazones, bridged by 1,2-bis(diphenylphosphino)ethane

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Square planar geometry;
Spectroscopic characterization

Abstract The work described in this paper involves the synthesis and structural characterization of Ni(II) complexes derived from dihydroxybenzaldehyde thiosemicarbazones (H_3L^1, H_3L^2, H_3L^3, H_3L^4) and 1,2-bis(diphenylphosphino)ethane (dppe). Ligands and their Ni(II) complexes were characterized by elemental analysis, IR, UV–Vis, (^{1}H, ^{13}C, ^{31}P) NMR, as well as magnetic moment and X-ray structure analysis. The results so obtained suggest that the thiosemicarbazone ligands behave as a tridentate ligand which were coordinated with Ni(II) ion through O, N and S atoms. Furthermore, the dppe ligand was coordinated with Ni(II) ion through the P atom. It is concluded that all Ni(II) complexes have a Square-planar geometry.

1. Introduction

The synthesis and characterization of Schiff base ligands have shown a wide range of biological and pharmaceutical activities such as antibacterial, anti-proliferative, antiviral, antimicrobial, antifungal, anti-inflammatory, anticonvulsant, antitubercular, antioxidative effects and inhibition of tumor growth (Abeer et al., 2012; Ahmed, 2009; Ali et al., 2006; Madalina et al., 2010; Vinuelas et al., 2008). Thiosemicarbazone derivatives are well known for their pharmacological activities and have received considerable attention over the past few years (Akbar and Tarafdar, 1977; Balwan and Harihar, 1986; Shayma et al., 2010a). Most of the thiosemicarbazone derivatives are used as chemical intermediates, perfume bases, dyes, rubber accelerators and liquid crystals for electronics (Abeer et al., 2011). Moreover, the hydrazine group has two imino and amino nitrogen atoms whose valance electrons differ in

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their degree of hybridization. In addition, complexes of the thiosemicarbazone derivatives display remarkable anti-inflammatory, antimutagenic, anticarcinogenic, antiallergic and antitumor activities against HL60 and A.549 cancer cell lines (Ling et al., 2008). In a mixed ligand system tridentate and monodentate ligands along with the oxygen atom would provide the penta coordinate environment to the metal center (Bipul et al., 2008). Moreover, hydrazine derivative complexes play an important role in inorganic and bioinorganic chemistry, since it has been recognized that many of these complexes may serve as models for biologically important species (Mostafa and Haifaa, 2007). Indeed, a great deal of research work has been carried out on the preparation and characterization of transition metal complexes with these ligands due to their applications in organic chemistry (Antonio et al., 2008). Furthermore, the presence of additional donor atoms in the ligand allows the formation of the stable chelate ring and this situation facilitates the complexation process (Antonio et al., 2008). In the present investigation we describe the preparation and characterization of Ni(II) complexes of Schiff base containing polyhydroxybenzaldehyde thiosemicarbazone, bridged by 1,2-bis(diphenylphosphino)ethane.

2. Experimental

2.1. Material and instrumentals

2,3-Dihydroxybenzaldehyde, thiosemicarbazide, 4-methyl-3-thiosemicarbazide, 4-ethyl-3-thiosemicarbazide, 4-phenyl-3-thiosemicarbazide, 1,2-bis(diphenylphosphino)ethane, potassium thiocyanate and Ni(II) acetate tetrahydrate were obtained from Sigma–Aldrich. $[NiCl_2(dppe)]$ was prepared following the literature procedure (Hecke et al., 1966). All the solvents used in the reaction were from Merck and used as received.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum RX-1 spectrophotometer as KBr pellets in the frequency range of 4000–400 cm^{-1}. NMR spectra were recorded in deuterated DMSO-d_6 on an ECA 400 MHz instrument. UV–Vis spectra were recorded with DMF solvent on a Shimadzu UV-1650PC spectrophotometer. Elemental analyses were performed on a Thermo Finnigan Eager 300 CHNS elemental analyzer. Magnetic susceptibilities were measured at 25 °C using a magnetic susceptibility balance, model MK1 (Sherwood Scientific, Cambridge, UK).

2.2. Synthesis of ligands

The thiosemicarbazone ligands were prepared by condensation of the corresponding N(4)-substituted thiosemicarbazide with 2,3-dihydroxybenzaldehyde following the published procedure (Swesi et al., 2007).

*2.3. Synthesis of complexes $[Ni(HL)_2(\mu\text{-dppe})]$ (**1**), (**2**) and (**3**)*

The following three complexes were prepared by a general method using $Ni(OAC)_2{\cdot}4H_2O$ as the starting material.

*2.3.1. $[Ni_2(HL^1)_2(\mu\text{-dppe})]$ (**1**)*

To a warm solution composed of 30 ml of methanol, 0.124 g (0.0005 mol) $Ni(CH_3COO)_2{\cdot}4H_2O$, 0.097 g (0.001 mol) KSCN and 0.2 g (0.0005 mol) dppe, was added 10 ml of boiling methanol containing 0.105 g (0.0005 mol) H_3L^1. The mixture was stirred under reflux for 4 h. The resulting orange precipitate (**1**) was filtered off, washed with ethanol and diethyl ether and dried at room temperature. Yield: 82% (0.19 g). Anal. Calc. for $C_{42}H_{38}N_6$ $Ni_2O_4P_2S_2$: C, 53.99; H, 4.10; N, 9.00; S, 6.86. Found: C, 53.76; H, 4.21; N, 9.09; S, 6.82%. ^{1}H NMR (DMSO-d_6, ppm): 8.22 (s, 1H, OH), 7.84 (s, 1H, —CH=N), 7.63–7.38 (m, 10H, dppe aromatic), 6.86 (1H, d, (J = 7.8), 6.63 (1H, d (J = 7.3), 6.56 (s, 2H, $-NH_2$), 6.43 (t, 1H), 2.82 (s, 2H, ($-CH_2-$). ^{13}C NMR (DMSO-d_6,ppm): 171.37, 149.96, 149.40, 147.67,133.08, 132.46, 131.55, 131.00, 129.39, 122.81, 117.82, 115.52, 113.97. ^{31}P NMR (DMSO-d_6): 22.03. IR (KBr disk, cm^{-1}): 3429 s, 3282 s, 3259 s, 3151 s, 2971 m, 1584 m, 1593 w, 1553 s, 1531s, 1457 s, 1437 m,1411w, 1304s, 1261 w, 1230 s, 1180 w, 1102 m, 1048 w, 982 s, 946 w, 877 m, 843 w, 778 m, 732 m, 722 s, 694 m, 592 w, 511 m, 483 m (s, strong; m, medium; w, weak).

*2.3.2. $[Ni_2(HL^2)_2(\mu\text{-dppe})]$ (**2**)*

Complex **2** was also prepared similarly to **1**, but replacing H_2L^1 by 0.112 g (0.0005 mol) H_2L^2. Yield: 89% (0.21 g). Anal. Calc. for $C_{44}H_{42}N_6$ $Ni_2O_4P_2S_2$: C, 54.92; H, 4.40; N, 8.73; S, 6.66. Found: C, 54.89; H, 4.41; N, 8.80; S, 6.62%. ^{1}H NMR (DMSO-d_6, ppm): 8.30 (s, 1H, OH), 7.71 (s, 1H, —CH=N), 7.63–7.36 (m, 10H, dppe aromatic), 6.93 (1H, d, (J = 7.8), $-\underline{NH}$CH3), 6.85 (1H, d (J = 7.7)), 6.60 (d, 1H, –(J = 7.2)), 6.41 (t, 1H), 2.78(s, 2H, ($-CH_2-$)), 2.66 (3H, d (J = 4.5)). ^{13}C NMR (DMSO-d_6, ppm): 170.58, 150.63, 149.39, 147.69, 133.12, 132.43, 131.52, 131.03, 129.39, 122.87, 117.95, 115.52, 114.03, 32.34. ^{31}P NMR (DMSO-d_6, ppm): 21.93. IR (KBr disk, cm^{-1}): 3436 s, 3259 s, 3052 s, 2945 m, 1590 s, 1555 s, 1530 s, 1531s, 1457 s, 1434 m,1408 m, 1304 m, 1228 s, 1167 m, 1101 m, 1065 w, 1048 w, 946 w, 872 m, 813 w, 778 w, 732 m, 704 m, 695 m 590 w, 558 w, 525 m, 476 m, 441 w (s, strong; m, medium; w, weak).

*2.3.3. $[Ni_2(HL^3)_2(\mu\text{-dppe})]$ (**3**)*

Complex **3** was also prepared under similar reaction condition of **1**, but replacing H_2L^1 by 0.119 g (0.005 mol) H_2L^3. Yield: 90% (0.22 g). Anal. Calc. for $C_{46}H_{46}N_6$ $Ni_2O_4P_2S_2$: C, 55.79; H, 4.68; N, 8.49; S, 6.48. Found: C, 55.76; H, 4.66; N, 8.45; S, 6.51%. ^{1}H NMR (DMSO-d_6, ppm): 8.32 (s, 1H, OH), 7.74 (s, 1H, —CH=N), 7.61–7.38 (m, 10H, dppe aromatic), 7.00 (t, 1H, $-\underline{NH}CH_2CH_3$), 6.89 (d, 1H, (J = 7.8)), 6.64 (1H, d (J = 7.3)), 6.44 (t, 1H), 3.15 (q, 2H, $\underline{CH_2}CH_3$), 1.03 (t, 3H, $CH_2\underline{CH_3}$), 2.79(s, 2H, ($-CH_2-$). ^{13}C NMR (DMSO-d_6,ppm): 169.69, 150.41, 149.39, 147.67, 133.12, 132.43, 131.55, 129.38, 122.85, 117.97, 115.51, 113.99. ^{31}P NMR (DMSO-d_6, ppm): 22.04. IR (KBr disk, cm^{-1}): 3434 m, 3400 m, 3050 m, 2968 m, 1596 m, 1559 s, 1534 s, 1459 s, 1435 m, 1306 m, 1261 m, 1231 s, 1155 w, 1102 m, 1043 w, 998 w, 872 m, 833 w, 777 w, 733 s, 718 s, 702 m 593 w, 556 m, 519 m, 489 m, 436 w (s, strong; m, medium; w, weak).

*2.3.4. $[Ni_2(HL^4)_2(\mu\text{-dppe})]$ (**4**)*

Solid $[NiCl_2(dppe)]$ (0.19 g; 0.0004 mol) was slowly added to H_3L^4 (0.104 g; 0.0004 mol) in ethanol/acetonitrile mixture (30 ml). The mixture was refluxed for 2 h. The dark red solution was allowed to stand for 4 days at room temperature. Yield: 87% (0.24 g). Anal. Calc. for $C_{54}H_{46}N_6Ni_2O_4P_2S_2$: C, 59.70; H, 4.27; N, 7.74; S, 5.90. Found: C, 59.73; H, 4.23; N, 7.79; S, 5.87%. ^{1}H NMR (DMSO-d_6, ppm): 9.41 (s, 1H, OH), 8.60 (s, 1H, —CH=N), 7.67 (d, 2H, phenyl), 7.49 (t, 2H, dppe aromatic), 7.40 (t, 4H, dppe aromatic), 7.22 (t, 2H, phenyl), 6.99 (dd,1H, NH-Ph), 6.88 (t, 2H, phenyl & aromatic), 6.72 (dd, 1H, aromatic(J = 7.6,1.2)), 6.49 (t, 1H, aromatic), 2.99 (s, 2H, (–CH$_2$–). ^{13}C NMR (DMSO-d_6,ppm): 166.24, 153.32, 150.47, 141.80, 133.18, 131.53, 129.41, 129.03, 123.29, 121. 76, 118.65, 117.82, 115. 76, 114.79. ^{31}P NMR (DMSO-d_6, ppm): 22.91. IR (KBr disk, cm^{-1}): 3426 s, 3052 m, 1594 s, 1593 w, 1559 s, 1508 s, 1455 s, 1434 s,1400 m, 1310 s, 1268 m, 1229 s, 1205 m, 1102 m, 1054 w, 982 s, 995 w, 873 m, 833 w, 778 w, 736 m, 717 m, 692 m, 590 w, 556 m, 520 m, 490 m, 447 w (s, strong; m, medium; w, weak).

2.4. X-ray crystallography

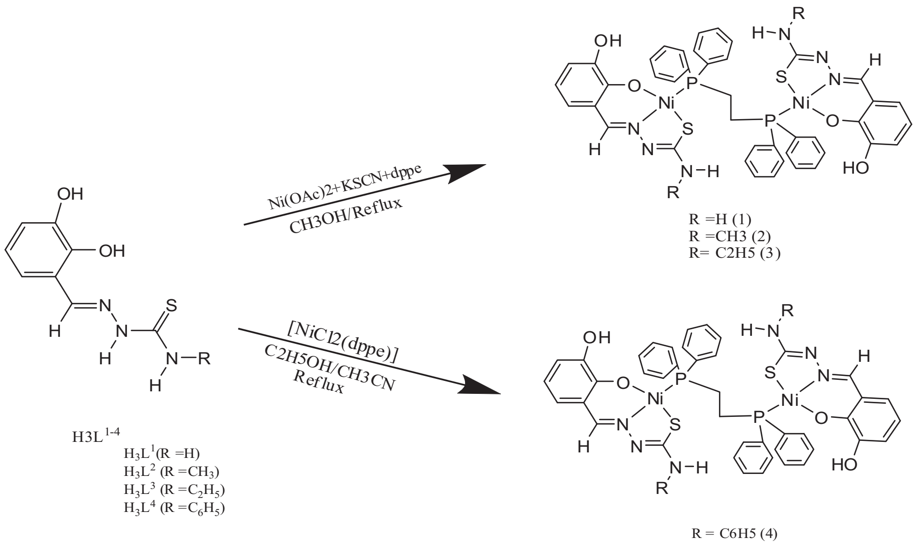
Crystals for complexes **1** and **2** were grown by recrystallization from dimethylformamide (DMF). Data of compounds **1** and **2** were collected using a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo Kα (Λ = 0.71073 Å) radiation. Absorption corrections on the data were made using SADABS (Sheldrick, 1996). Structures were solved and refined by SHELXL97 (Sheldrick, 2008). Molecular graphics were drawn by using ORTEP (Farrugia, 1997) and PLATON (Spek, 2003). Material for publication was prepared using publCIF. Structures were solved by direct-methods and refined by a full-matrix least-squares procedure on F^2 with anisotropic displacement parameters for non-hydrogen atoms.

3. Result and discussion

Binuclear nickel complexes of thiosemicarbazones (**1**–**4**) of the general formula, [Ni$_2$(HL)$_2$(μ-dppe)] where dppe = 1,2-bis(diphenylphosphino)ethane; HL = doubly deprotonated 2,3-dihydroxybenzaldehyde-N4-substituted thiosemicarbazone were formed in excellent yields by the reaction of ligands with nickel(II) acetate and dppe in methanolic solution. However, the complex [Ni$_2$(HL^3)$_2$(μ-dppe)] (HL^3 = 2,3-dihydroxybenzaldehyde-N4-phenyl substituted thiosemicarbazone) was formed by the reaction of the ligand with [NiCl$_2$(dppe)] in acetonitrile/ethanol mixture (Scheme 1). The spectroscopic and crystallographic data show that all these complexes are dinuclear where the two nickel(II) ions are bridged by the bidentate dppe ligand. The prepared complexes were found to be solid, insoluble in water but they were soluble in some organic solvents such as dimethylformamide and dimethylsulfoxide. The magnetic moment values of all nickel(II) thiosemicarbazone complexes in the crystalline state show diamagnetic nature and the results are in accordance with a square planar geometry for d^8 system (Boettcher et al., 1993).

3.1. The IR spectral studies

The infrared spectra of ligands and their Ni(II) complexes were recorded and compared with those of the free ligands in order to clarify the mode of bonding. The characteristic absorption of all complexes shows bands at 3426–3436 cm^{-1} which corresponded to the v(OH) (Han and Shao, 2006). Actually, the diprotic thiosemicarbazone ligands H3L^1, H3L^2, H3L^3 and H3L^4 can be found as thione or thiol forms tautomerism (H—N—C=S) and (C=N—SH). Metal coordination of Ni(II) complexes, however occurs through sulfur in thiol form via deprotonation of the –SH group (Shayma, 2010b). In addition, upon complexation the band of v(C–S) was shifted to lower frequencies by 21–18 cm^{-1} providing strong evidence for the coordination of thiosemicarbazone ligands to nickel(II) ion in the deprotonated thiolate form (Campbell, 1975). Moreover, in the ligand spectra, the strong band observed at around 1611–1590 cm^{-1} is assigned to (C=N) stretching vibration which also underwent a change in frequency and intensity, caused by complexation. This band shifts to a higher frequency by 10–50 cm^{-1} in all complexes, indicating the coordination of nitrogen of the azomethine group to the nickel ion (Ali et al.,



Scheme 1 Schematic representation of ligands H$_3$L$^{1–4}$ and the synthesis of mixed nickel(II)–dppe complexes of polyhydroxybenzaldehyde.

2011). Moreover, spectra of all complexes exhibit an increase by 50–30 cm^{-1}in the frequency of ν(N–N) bands, which was found in the region 1070–1043 cm^{-1} of the free ligands (Ali et al., 2011; Youssef et al., 2009). This blue shift is due to the decrease in the repulsion between the lone pairs on the two nitrogen atoms. It is noted that the ν(C–O) was shifted to lower frequencies by 23–17 cm^{-1} respectively on Ni(II) complexes (Ana et al., 1999; Nakamoto, 1997; Shayma, 2010c). On the other hand, spectra of Ni(II) complexes exhibited new bands at (556–592), (511–525) and (436–490) cm^{-1} which were attributed to ν(Ni–N), ν(Ni–O) and ν(Ni–S), respectively which indicates that the Ni(II) ion is coordinated through the azomethine N, thiol S and phenolic oxygen, on loss of the OH proton (Aboelfetoh et al., 1998; Douglas et al., 1997). The presence of dppe in all complexes is confirmed by the presence of characteristic strong two bands with almost equal intensity assigned for bridging dppe in the region 740–690 cm^{-1} (Vijayshree et al., 1993).

3.2. Electronic spectral studies

UV spectra of ligands show essential bands in the range of 274–280 and 321–361 nm which were attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively. Thus, spectra show bands which appear at longer wavelength as expected from the higher aromaticity of ligands which eases delocalization of electron density. On the other hand, the electronic absorption spectra of Ni(II) complexes are characterized by a broad band at the range of 353–359 and 405–414 nm which may be assigned to two allowed transitions $^1A_1g_{(D)} \rightarrow {}^1Eg_{(G)}$ and $^1A_1g_{(D)} \rightarrow {}^1B_2g_{(G)}$, respectively. Moreover, at room temperature these complexes show a diamagnetic behavior which indicates the square planar environment around the Ni(II) ion (Chandra et al., 2009; Lever, 1968; Prakash et al., 2011; Shayma, 2010c,d).

3.3. ^{1}H NMR spectral studies

^{1}H NMR spectra of ligands show signals in 8.95–9.55 ppm attributed to two OH. This signal appeared in Ni(II) complexes at 8.22–9.41 ppm. However, the integration of this signal in complexes is attributed to one OH confirming the coordination of only one phenolic oxygen to Ni(II). In addition, the azomethine proton —CH=N does not show a regular trend in complexes. The azomethine —CH=N signals observed at 8.33–8.52 ppm in the free thiosemicarbazones undergo shift to the high field in complexes **1**, **2** and **3** to 7.71–7.84 ppm. In contrast, the azomethine proton in complex **4** is shifted downfield to 8.60 ppm due to the presence of an electron withdrawing phenyl group. Furthermore, the signal appeared at 11.35–11.77 ppm in the free ligands, which attributed to the NHCS was disappeared in the spectra of the Ni(II) complexes indicating the coordination of the ligand under the anionic thiolate form upon deprotonation at N(2) (Lobana et al., 2010). That the absence of the signal proton of the SH group caused deprotonation is further supported by the presence of the thiol form in the complexes instead of thione form. Moreover, spectra of complexes show bands at 7.22–7.63 ppm which were attributed to phenyl protons of the dppe ligand.

3.4. ^{13}C NMR spectral studies

^{13}C NMR spectra of ligands H_3L^1, H_3L^2, H_3L^3 and H_3L^4 in DMSO-d_6 showed proton signals δ(176.19–178.04), (145.17–146.08) and (139.78–141.25) ppm which were attributed to C–S, C–O and C=N, respectively. In the diamagnetic Ni(II) complexes the bands of C–S were shifted upwards at 166.24–171.37. Nevertheless, the signal of C–O and C=N was shifted downwards at 149.39–153.32 and 147.67–147.67 ppm, respectively. These signals indicate that ligands were coordinated with metal ion through the O, N and S atoms.

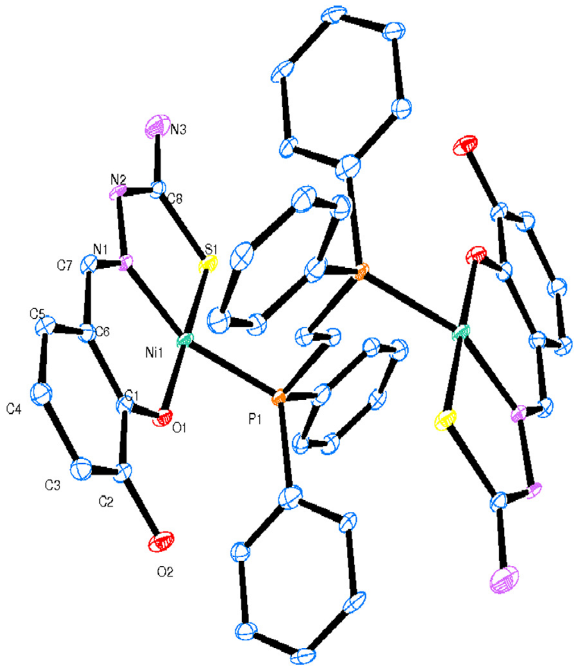


Figure 1 Crystal structure of complex **1**. The thermal ellipsoids are plotted at the 30% probability level. Hydrogen atoms and DMF solvent are omitted for clarification.

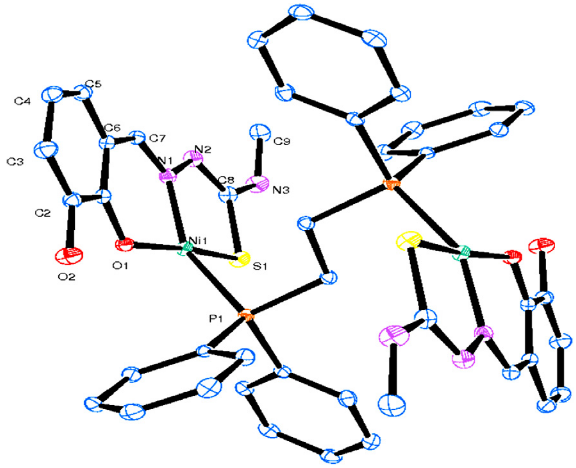


Figure 2 Crystal structure of complex **2**. The thermal ellipsoids are plotted at the 30% probability level. Hydrogen atoms and DMF solvent are omitted for clarification.

Table 1 Crystal data and structural refinement for compounds **1** and **2**.

Parameters	$[Ni_2(HL^1)_2(dppe)]\cdot DMF$ **(1)**	$[Ni_2(HL^2)_2(dppe)]\cdot DMF$ **(2)**
Empirical formula	$C_{48.03}H_{60.01}N_8Ni_2O_6\cdot 60P_2S_2$	$C_{42.37}H_{54.59}N_{14}Ni_2O_6P_2S_2$
Formula weight, M	1086.21	1108.51
Temperature, T (K)	100	100
Wavelength, Mo Kα (Å)	$\lambda = 0.71073$	$\lambda = 0.71073$
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Unit cell dimensions		
a (Å)	10.1334(2)	10.35810(10)
b (Å)	10.1645(2)	10.62240(10)
c (Å)	12.7332(3)	12.5820(2)
α (°)	80.107(2)	101.0720(10)
β (°)	71.727(2)	102.3060(10)
γ (°)	80.387(2)	108.0400(10)
Volume V ($Å^3$)	1217.87(4)	1235.46(3)
Z	1	1
Absorption coefficient, μ (mm^{-1})	0.983	0.970
Crystal size (mm)	$0.14 \times 0.17 \times 0.17$	$0.180 \times 0.160 \times 0.12$
Reflections collected	10,839	11,024
Density (calculated), (mg m^{-3})	1.481	1.490
$F(000)$	565	578
Data/parameters/restraints	4981/340/0	5072/318/0
S	0.971	1.059
Independent reflections	4981 [R(int) = 0.0660]	5072 [R(int) = 0.0322]
$R[F^2 > 2\sigma(F^2)]$	0.0469	0.0644
$wR(F^2)$	0.1288	0.1496
Largest difference peak and hole (e $Å^{-3}$)	0.001 and 0.000	0.141 and 0.003

3.5. ^{31}P NMR spectral studies

^{31}P NMR spectrum of the free ligand 1,2-bis(diphenylphosphino)ethane exhibited one peak shifted upfield from zero (−11.92) ppm. This band was shifted downfield in Ni(II) complexes by 10.01–10.99 ppm. As phosphorus sigma donates electron density along the P–M bond, this causes deshielding at the phosphorus atom. The downfield shift seen in the ^{31}P NMR spectra supports the conclusion that P–M bond had formed.

3.6. Crystal structure of complexes *1* and *2*

Complexes $[Ni_2(HL^1)_2(dppe)]$. DMF (**1**) and $[Ni_2(HL^2)_2(dppe)]$. DMF (**2**) were crystallized in the triclinic crystal system with *P*-1 space group. A summary of the crystallographic data for complexes **1** and **2** collected at 100 K is gathered in Table 1. Figs. 1 and 2 illustrate the structural features of complexes **1** and **2**, respectively, for which selected bond lengths and bond angles are listed in Table 2. In both complexes, the asymmetric unit of the crystal of these complexes consists of one Ni(II) ion, one thiosemicarbazone ligand, half 1,2-bis(diphenylphosphine)ethane, (dppe), as well as a DMF molecule. Thus, the dppe ligand bridges two Ni(II) ions forming a dinuclear complex. The doubly deprotonated thiosemicarbazone ligand behaves as a tridentate ligand coordinate to nickel(II) via thiolate sulfur, azomethine nitrogen atom, as well as phenolic oxygen. In comparison with bond lengths in coordinated 2,3-dihydroxybenzaldehyde thiosemicarbazone and 2,3-dihydroxybenzaldehyde-N4-methylthiosemicarbazone ligands with the related free ligands (Farina and Simpson, 2008; Swesi et al., 2006), shortening of the C8–N2 bond distance, and lengthening of C7–N1, C8–S1 bond lengths within the five-membered chelate ring are observed, consequent upon dissociation of the hydrazinic proton (Acharyya et al., 2006). The C7–N1 bond length of 1.297(4) Å and 1.306(5) Å, for **1** and **2**, respectively, and C8–S1 bond length of 1.753(3) Å and 1.760(4) Å, for **1** and **2**, respectively, are similar to those reported for coordinated thiosemicarbazone in the thiolate form (Kolotilov et al., 2007; Lobana et al., 2007).

In complex **1** each Ni(II) ion lies on a square planar coordination NiSNOP with a P–Ni–N bond angle 155.10(9) and O–Ni–S bond angle 174.82(8) deviating considerably from the ideal angle of 180°. The Ni(II) ion is found to be displaced by 0.175 Å from the plane constituting atoms N1, S1, O1 and P1. The two thiosemicarbazone ligands in the dimer are approximately trans around the Ni(II)–(μdppe)–Ni(II) fragment. The Ni–S bond length of the coordinated thiosemicarbazone ligand of 2.1343(9) Å is shorter than the Ni–P bond length of the dppe 2.1774(9) Å. This indicates that the bonding is dominated by thiosemicarbazone moiety. Ni–S, Ni–N and Ni–O distances of 2.1343(9), 1.891(3) and 1.851(2) Å, respectively, are comparable with values reported for similar structures (Latheef and Kurup, 2008; Güveli et al., 2009).

Similar to complex **1**, Ni(II) in complex **2** adopts a square planar geometry defined by the tridentate ONS donor dianionic ligand and neutral bidentate dppe ligand which occupy the fourth coordination site and bridge two nickel ions in the dimer. The Ni–O, Ni–N and Ni–S bond lengths [Nil–Ol, 1.856(2); Ni1–N1, 1.892(3); Nil–S1, 2.1416(4)); Nil–P1, 2.1722(10)] are in agreement with complex **1** and those found in the related Ni(1I) complex. The C7–N1 and N2–C8 bond lengths are comparable to those of C=N bond length. Of these two, N2–C8 bond length is larger due to enolization of the ligand in complex formation. The Sl–Ni1–N1 and

Table 2 Selected bond lengths (Å) and bond angles (°) of compounds **1**and **2**.

Complex **1**		Complex **2**	
Bond lengths		*Bond lengths*	
O1–Ni1	1.851(2)	O1–Ni1	1.856(2)
C7–N1	1.297(4)	C7–N1	1.306(5)
N1–N2	1.398(4)	N1–N2	1.401(4)
Ni1–S1	2.1343(9)	Ni1–S1	2.1416(4)
N1–Ni1	1.891(3)	N1–Ni1	1.892(3)
N2–C8	1.297(5)	N2–C8	1.308(4)
C8–N3	1.344(5)	C8–N3	1.344(5)
C8–S1	1.753(3)	C8–S1	1.760(4)
Ni1–P1	2.1774(9)	Ni1–P1	2.1722(10)
P1–C9	1.809(4)	P1–C10	1.819(4)
P1–C15	1.817(3)	P1–C16	1.809(4)
P1–C21	1.826(3)	P1–C22	1.827(3)
C2–O1–Ni1	125.3(2)	C1–O1–Ni1	124.8(2)
O1–C1–C2	125.6(3)	O1–C1–C2	116.1(3)
O1–C2–C3	116.6(3)	O1–C1–C6	125.0(3)
N1–C7–C1	125.9(3)	N1–C7–C6	126.0(3)
C7–N1–N2	113.5(3)	C7–N1–N2	113.9(3)
C7–N1–Ni1	124.9(2)	C7–N1–Ni1	124.2(3)
N2–N1–Ni1	121.4(2)	N2–N1–Ni1	121.6(2)
C8–N2–N1	112.3(3)	C8–N2–N1	112.0(3)
N2–C8–N3	118.9(3)	N2–C8–N3	120.1(4)
N2–C8–S1	122.5(3)	N2–C8–S1	122.9(3)
N3–C8–S1	118.6(3)	N3–C8–S1	117.0(3)
C8–S1–Ni1	96.36(12)	C8–S1–Ni1	96.13(13)
O1–Ni1–N1	95.51(11)	O1–Ni1–N1	95.30(12)
O1–Ni1–S1	174.82(8)	O1–Ni1–S1	173.52(8)
N1–Ni1–S1	87.40(9)	N1–Ni1–S1	87.35(9)
O1–Ni1–P1	88.28(8)	O1–Ni1–P1	88.08(8)
N1–Ni1–P1	155.10(9)	N1–Ni1–P1	155.22(9)
S1–Ni1–P1	90.87(4)	S1–Ni1–P1	91.99(4)
C15–P1–Ni1	122.02(11)	C16–P1–Ni1	123.21(12)
C9–P1–Ni1	118.24(12)	C10–P1–Ni1	117.22(12)
C21–P1–Ni1	99.93(11)	C8–N3–C9	121.9(3)

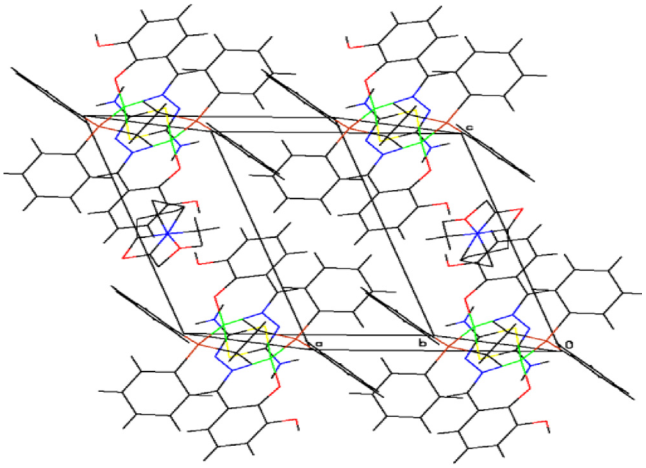


Figure 4 Unit cell packing diagram of compound **1**.

P1–Ni1–N1 bond angles indicate a slight tilting of the Ni1–S1 bond in the direction of Ni1–N1 bond and away from the P1–Ni1 bond. The bite angle S–Ni–O of 173.52(8)° and N–Ni–P of 155.22(9)° defines considerable distortion from the square planar geometry. This deviation from an ideal stereochemistry may be due the restricted bite angle imposed by both the HL^{2-} and dppe ligands.

In compounds **1** and **2**, one molecule of DMF moiety is present in the crystal lattice, which is hydrogen bonded to the hydrogen atom (H3) of the N(3) amino group of adjacent complex molecule. Moreover, in complex **1**, intermolecular hydrogen bonding interactions were observed, Fig. 3, *i.e.*, N3(H) of one molecule with the nitrogen atom (N2) of the another molecule. In compound **1** there are 4 molecules in the unit cell packing and the molecules are complement to one another, (Fig. 4). In case of complex **2**, two molecules are present and two of them are parallel to each other, (Fig. 5).

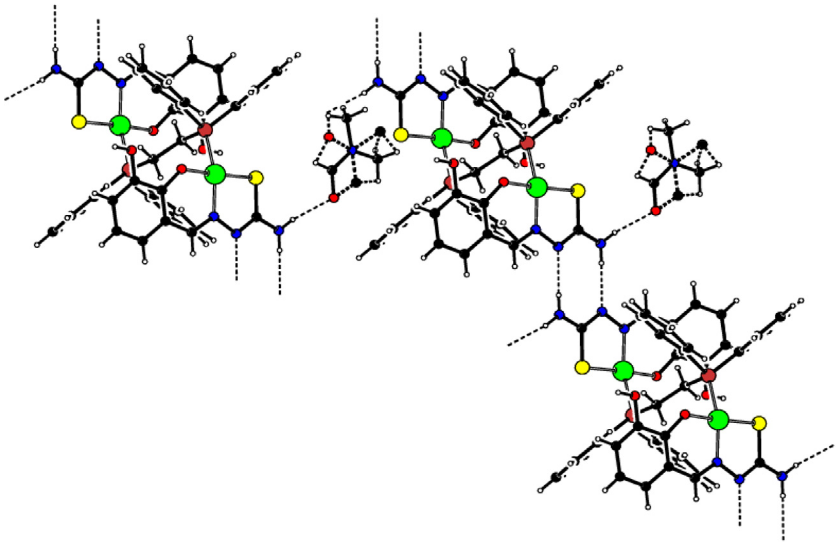


Figure 3 Intermolecular hydrogen bonding interactions of **1**.

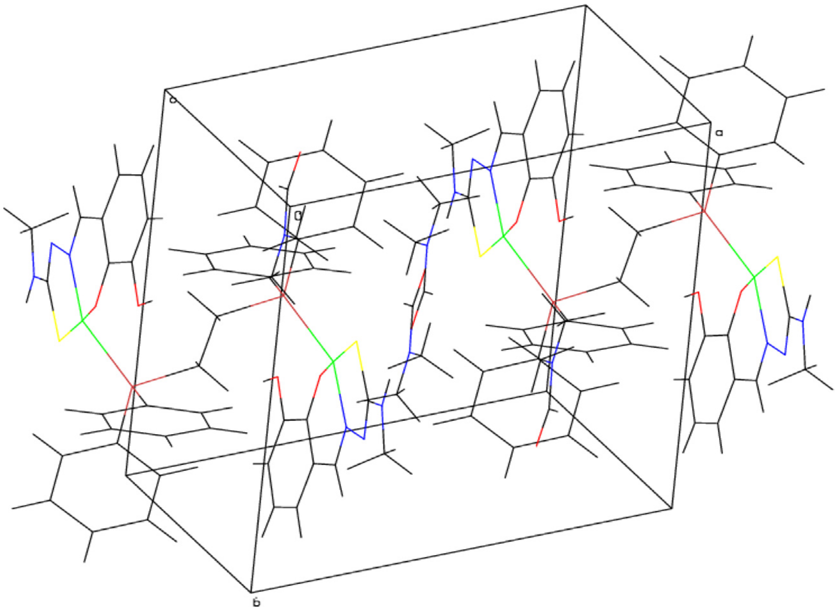


Figure 5 Unit cell packing diagram of complex **2**.

4. Conclusion

New 2,3-dihydroxybenzaldehyde thiosemicarbazone complexes were synthesized by the reaction of the Ni(II) ion with ligands H_3L^1, H_3L^2, H_3L^3, H_3L^4 and 1,2-bis(diphenylphosphino)ethane (dppe), with the molar ratio 1:2:1 (Ni:H_3L:dppe). The thiosemicarbazone derivative ligands and their Ni(II) complexes were characterized by elemental analysis, IR, UV–Vis, (^{1}H, ^{13}C, ^{31}P) NMR, as well as magnetic moment and X-ray structure analysis. In Ni(II) complexes the appearance of ν(C=N–N=C) and ν(C–S) indicates that the Ni(II) ion is bonded to ligands through N and S atoms. The coordination of ligands through O atom is confirmed by the down shift of the ν(C–O). Moreover, UV–Vis spectra of Ni(II) complexes showed absorption bands between 353 and 414 nm which indicate that nickel is in a square planar geometry.

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