DOI: 10.1002/zaac.201200012

Pyrrole-2-carbaldehyde Thiosemicarbazonates of Nickel(II) and Palladium(II): Synthesis, Structure, and Spectroscopy

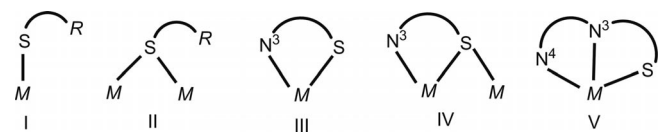
Tarlok S. Lobana,*[a] Poonam Kumari,[a] Gagandeep Bawa,[a] Geeta Hundal,[a] Ray J. Butcher,[b] Francisco J. Fernandez,[c] Jerry P. Jasinski,[d] and James A. Golen[d]

Keywords: Thiosemicarbazone; Nickel; Palladium; Bis(diphenylphosphanyl)methane; Bipyridine

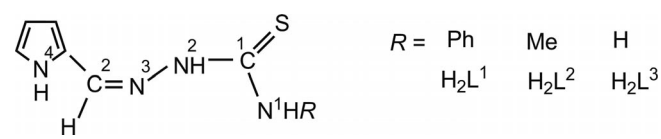
Abstract. Complexes of pyrrole-2-carbaldehyde thiosemicarbazones, [($C_4H_4N^4$)(H)C^2=N^3–N^2(H)–C^1(=S)–N^1H*R*; *R* = Ph, H_2L^1; Me, H_2L^2; H, H_2L^3] with nickel(II) and palladium(II) are described. The reaction of nickel(II) acetate with H_2L^1 in methanol in 1:1 molar ratio yielded a complex of composition, [Ni(κ^2-N^3,S-HL^1)$_2$] (**1**). Likewise reaction of $NiCl_2$ with H_2L^2 in 1:1 molar ratio in acetonitrile in the presence of triethylamine base followed by the addition of pyridine did not yield the anticipated [Ni(κ^3-N^4,N^3,S-L^2)(py)] complex, moreover a bis-square-planar complex, [Ni(κ^2-N^3,S-HL^2)$_2$] (**2**) was formed. However, in the presence of bipyridine (bipy), it yielded the addition product, [Ni(κ^2-N^3,S-HL^2)$_2$(κ^2-N,N-bipy)] (**3**). Reaction of $PdCl_2$(κ^2-P,P–PPh_2–CH_2–PPh_2) with H_2L^3 in toluene in the presence of triethylamine has yielded a complex of stoichiometry, [Pd(κ^3-N^4,N^3,S–L^3)(κ^1-P–PPh_2–CH_2–P(O)Ph_2] (**4**). The ligands $(HL^1)^-$ and $(HL^2)^-$ are chelating to Ni^{II} metal atom as anions binding through N^3,S-donor atoms with pendant pyrrole groups, and $(L^3)^{2-}$ is chelating to the Pd^{II} metal atom as dianion through N^4,N^3,S-donor atoms (pyrrole is N^4-bonded). Fourth site in **4** is bonded to one P-donor atom of PPh_2–CH_2–P(O)Ph_2, whose pendant –PPh_2 group involves auto oxidation to –P(O)PPh_2 during reaction. These complexes were characterized using analytical data, IR, NMR (^{1}H, ^{31}P) spectroscopy and X-ray crystallography. Complexes **1**, **2**, and **4** have square-planar arrangement, whereas complex **3** is octahedral.

Introduction

Thiosemicarbazones [$R^1R^2C^2$=N^3–N^2(H)–C^1(=S)–N^1HR^3] are an important class of thio-ligands with biological relevance,[1–3] they display variable bonding modes, which lead to different metal-organic frameworks, metal-sensing properties, and other analytical applications.[4–6] Pyrrole-2-carbaldehyde thiosemicarbazones (H_2L) have shown different bonding modes. Modes I and II are observed in mononuclear Zn^{II}, Cd^{II}, and dinuclear Cu^{I}, Ag^{I}, and Hg^{II} complexes.[7] In these complexes the thio ligands are neutral. The uninegative thio ligands exhibit modes III and IV in mononuclear Ni^{II}, Pd^{II}, Au^{III}, or Hg^{II} complexes.[8] Mode V is observed in square planar Pd^{II} complexes, where thio ligands are dinegative.[9] The pyrrole ring remained pendant in modes I–IV, whereas it is coordinating in mode V.



It has to be noted here that as mentioned above, Ni^{II} and Pd^{II} metal atoms have formed bis square-planar complexes in the absence of any co-ligand.[8] Pd^{II} has formed a square-planar complex of type, [PdL(PPh_3)], in the presence of PPh_3 co-ligand.[9] However, there is no report of a Ni^{II} complex with pyrrole-2-carabaldehyde thiosemicarbazones in the presence of either P-donor or N-donor co-ligands.[5] In this paper, Ni^{II} and Pd^{II} coordination chemistry with pyrrole-2-carbaldehyde thiosemicarbazones in the presence of P-donor ($Ph_2PCH_2PPh_2$, dppm) and N-donor (pyridine, bipyridine) co-ligands was pursued.



Experimental Section

Materials and Techniques: Metal salts $Ni(OAc)_2$, $PdCl_2$, $NiCl_2$, thiosemicarbazide, *N*-methyl thiosemicarbazide, *N*-phenyl thiosemicarbazide, pyrrole-2-carbaldehyde, bis(diphenyl-phosphanyl)methane,

* Prof. Dr. T. S. Lobana
E-Mail: tarlokslobana@yahoo.co.in
[a] Department of Chemistry
Guru Nanak Dev University
Amritsar-143 005, India
[b] Department of Chemistry
Howard University
Washington DC 20059, USA
[c] Department of Structural and Quantitative Biology
Center for Biological Research (CIB–CSIC)
Ramiro de Maeztu 9
28040 Madrid, Spain
[d] Department of Chemistry
Keene State College
229 Main Street
Keene, NH 03435–2001, USA

Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201200012** or from the author.

Zeitschrift für anorganische und allgemeine Chemie ZAAC Journal of Inorganic and General Chemistry

pyridine, bipyridine, and Et_3N were purchased from Sigma–Aldrich Ltd. The ligands H_2L^1, H_2L^2, and H_2L^3 were synthesized by conventional procedures.[10] C, H, and N analyses were carried out with a thermoelectron FLASHEA1112 analyzer. The melting points were determined with a Gallenkamp electrically heated apparatus. The IR spectra were recorded using KBr pellets with a Varian 666-IR FT-IR spectrometer. The magnetic susceptibility of complex **3** was recorded with Magnetic Susceptibility balance by Johnson Matthey, Catalytic Systems Division Equipment. The ^{1}H NMR spectra were recorded with a JEOL AL300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as the internal reference. The ^{31}P NMR spectra were recorded at 121.5 MHz with $P(OMe)_3$ as the external reference taken as zero position.

Synthesis of Complexes

[Ni(κ²-N³,S-HL¹)₂] (1): To a colorless solution of H_2L^1 (0.200 mmol) in methanol (10 mL) was added solid $Ni(OAc)_2$ (0.100 mmol). The color of the solution changed to dark red and it was stirred for about 4 h. The clear solution after filtration was left for crystallization. Slow evaporation of the solution at room temperature gave brown crystals. Yield 71 %; M.p. 226–230 °C. $C_{24}H_{22}N_8NiS_2$: calcd. C 52.81; H 4.03; N 20.54 %; found: C 52.97; H 4.27; N 20.62 %. **IR** (KBr, selected absorption bands): ν(N¹–H) 3428 br; ν(N⁴–H) 3316 s; ν(C–H) 3061 m, 2995m; ν(C=N) + ν(C=C) 1598 s, 1542 s; ν(C–N) 1020 s; ν(C–S) 750s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 10.78 (s, 2 H, N⁴H), 7.41 (s, 2 H, C²H), 7.36 (m, 4 H, *o*-H), 7.26 (m, 6 H, *p*- and *m*-H), 6.72 (2 H, sb, C⁶H), 6.63 (2 H, sb, N¹H), 6.53 (m, 2 H, C⁴H), 6.17 (m, 2 H, C⁵H) ppm.

[Ni(κ²-N³,S-HL²)₂] (2): To a light green solution of $NiCl_2{\cdot}6H_2O$ salt (0.025 g, 0.105 mmol) in CH_3CN was added solid H_2L^2 (0.018 g, 0.105 mmol) followed by the addition of Et_3N base (1 mL) and stirred for 6h. A brown colored compound got separated during stirring along with the formation of $Et_3NH^+Cl^-$ salt. This compound was filtered and dried. Analytical data supported the formation of complex of stoichiometry, {NiL²} (Anal. for $C_7H_8NiN_4S$: calcd. C 35.19; H 3.35; N 23.46 %; found: C 34.93; H 4.31; N 23.84 %). To a suspension of {NiL²} (0.025 g, 0.111 mmol) in acetonitrile was added pyridine (0.5 mL) and stirred until a clear solution was obtained. The slow evaporation of this solution gave black crystals. Yield 75 %; M.p. 240–242 °C. $C_{14}H_{18}N_8NiS_2$: calcd. C 39.89; H 4.27; N 26.59 %. found: C 40.12; H 4.22; N 26.78 %. **IR** (KBr, selected absorption bands): ν(N¹–H) 3411 br; ν(N⁴–H) 3308 s; ν(C–H) 2995 m, 2876 m; ν(C=N) + ν(C=C) 1578 s, 1502 s; ν(C–N) 1035 s; ν(C–S) 767 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 11.13 (2 H, sb, N⁴H), 7.22 (s, 2 H, C²H), 6.96 (s, 2 H, C⁶H), 6.53 (t, 2 H, C⁴H), 6.22 (dd, 2 H, C⁵H), 4.90 (s, 2 H, N¹HMe), 2.98 (d, 6 H, CH_3) ppm.

[Ni(κ²-N³,S-HL²)₂(κ²-N,N-bipy)] (3): To a suspension of {NiL²} (0.025 g, 0.111 mmol) in acetonitrile was added solid bipyridine (0.17 g, 0.111 mmol) and stirred until a clear solution was obtained. Slow evaporation of this solution gave red-brown crystals. Yield 73 %; M.p. 160–162 °C. $C_{24}H_{26}N_{10}NiS_2$: calcd. C 49.88; H 4.50; N 24.25 %. found: C 50.02; H 4.42; N 24.43 %. **IR** (KBr, selected absorption bands): ν(N¹–H) 3421 br; ν(N⁴–H) 3317 s; ν(C–H) 3098 w, 3054 w, 3022 w, 2928 m, 2850 w; ν(C=N) + ν(C=C) 1598 s, 1494 s; ν(C–N) 1018 s, 963 s; ν(C–S) 762 s cm^{-1}. Electronic absorption spectrum (0.5×10^{-4} M in DMSO, λ_{max} /nm, ε /L·mol^{-1}·cm^{-1}): 413 (0.96×10^4), 374 (1.89×10^4), 353 (2.14×10^4), 333 (2.01×10^4), 307 (1.68×10^4), 294 (2.00×10^4), 275 (2.50×10^4). Magnetic moment: μ_{eff} = 2.98 BM.

[Pd(κ³-N⁴,N³,S-L³)(κ¹-P-PPh₂–CH₂–P(O)Ph₂)]·C₇H₈ (4): To $PdCl_2(\kappa^2\text{-P,P–}Ph_2P\text{–}CH_2\text{–}PPh_2)$ (0.05, 0.09 mmol) suspended in toluene was added H_2L^3 (0.02, 0.09 mmol) followed by Et_3N (2 mL) and solution stirred for 4 h. The $Et_3NH^+Cl^-$ salt separated at the bottom. It was filtered to remove $Et_3NH^+Cl^-$ and allowed to evaporate at room temperature which led to the formation of bright red crystals. Yield 70 %; M.p. 160–162 °C. $C_{31}H_{28}N_4OP_2PdS{\cdot}C_7H_8$: calcd. C 59.6; H 3.70; N 7.32 %. found: C 59.76; H 4.70; N 7.47 %. **IR** (KBr, selected absorption bands): ν(N–H) 3360 s, 3307 s; ν(C=N) + δNH_2 + ν(C=C) 1643 s, 1556 s; ν(P–C_{Ph}) 1099 s, ν(C–S) 784 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 7.96–7.60 (m, 8 H, *o*-H), 7.46–7.24 (m, 13 H, *m*-and *p*-H and C⁴H), 6.29 (q, 1 H, C⁵H), 6.49 (t, 1 H, C⁶H), 6.85 (t, 1 H, C⁷H), 7.08 (d, 1 H, C⁸H), 5.79 (m, 1 H, C⁵H), 5.62 (s, 1 H, C²H), 4.60 (s, 2 H, -NH_2), 3.50 (t, 2 H, CH_2). **^{31}P NMR** ($CDCl_3$): δ = –90.0, –83.4 ppm; coordination shift, $\Delta\delta(\delta_{complex}-\delta_{dppm})$ = 40.2.

Ligands Used

Pyrrole-2-carbaldehyde-*N*-phenyl Thiosemicarbazone (H_2L^1): Color: brown (67 %, M.p. 163–165 °C). **IR** (KBr, selected absorption bands): ν(N¹–H) 3354br; ν(N²–H) 3254 m; ν(N⁴–H) 3202 br; ν(C–H) 3007 m, 2975 m; ν(C=N) + ν(C=C) 1614 s, 1545 s; ν(C–N) 1089 s, 1035 s, 914 s; ν(C = S) 795 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 9.38 (s, 1 H, N²H), 9.04 (s, 2 H, N⁴H + N¹H), 7.71 (s, 1 H, C²H), 7.61 (d, 2 H, *o*-H), 7.29 (m, 3 H, *m*- and *p*- H), 6.94 (t, 1 H, C⁶H), 6.56 (s, 1 H, C⁴H), 6.29 (q, 1 H, C⁵H) ppm.

Pyrrole-2-carbaldehyde-*N*-methyl Thiosemicarbazone (H_2L^2): Color: brown (83 %, M.p. 175–177 °C). **IR** (KBr, selected absorption bands): ν(N¹–H) 3393br; ν(N²–H) 3242br; ν(N⁴–H) 3178br; ν(C–H) 2995 m, 2935 m, 2902 w; ν(C=N) + ν(C=C) 1543 s, 1514 s; ν(C–N) 1082 s, 1048 s, 927 s; ν(C=S) 800 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 10.42 (1 H, sb, N²H), 10.24 (1 H, db, N⁴H), 8.06 (1 H, sb, N¹H), 7.76 (s, 1 H, C²H), 6.87 (s, 1 H, C⁶H), 6.43 (s, 1 H, C⁴H), 6.19 (d, 1 H, C⁵H), 3.12 (d, 3 H, CH_3) ppm.

Pyrrole-2-carbaldehyde Thiosemicarbazone (H_2L^3): M. p. 194–196 °C.

X-ray Crystallography

A single crystal was mounted on a glass fiber and used for data collection with a Bruker SMART APEXII CCD area detector (**1**), Xcalibur, Eos, Gemini (**2**), Xcalibur, Ruby, Gemini (**3**) and Siemens P4 (**4**) diffractometers equipped with graphite monochromated Cu-K_α radiations in **1** (λ = 1.54178 Å) and with Mo-K_α radiations in **2**–**4** (λ = 0.71073 Å). Crystal data were collected at 100(2) (**1**) 170(2) (**2**) and 123(2) (**3**), and 295(2) (**4**) K. The data were processed with APEX2 and a multi-scan absorption correction was applied using SADABS[11] for complex **1**. For **2** and **3**, data were processed with CrysAlisPro and corrected for absorption using CrysAlisRED.[12] The data for **4** were processed with Siemens software and a psi-scans absorption correction was applied.[13] The structures were solved by direct methods using the program SHELXS-97 in the SHELXTL-PC[14] or SIR-92[15] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97[16] in the SHELXTL-PC[14] or WinGX package.[17] All non-hydrogen atoms in all structures were refined anisotropically. The hydrogen atoms were placed at the calculated positions except for amine hydrogen atoms in **2** and **3**, which were located from the difference Fourier and were refined isotropically with a thermal parameter of 1.2 times that of the carrier nitrogen atoms. Their bond lengths were also needed to be restrained [0.86(2) Å] in **2**. The complex **4** also shows the presence of a disordered toluene molecule in the asymmetric unit. This disorder could be resolved for the phenyl ring with 52 and

Table 1. Crystallographic data for compounds **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{24}H_{22}N_8NiS_2$	$C_{14}H_{18}N_8NiS_2$	$C_{24}H_{26}N_{10}NiS_2$	$C_{38}H_{36}N_4OP_2PdS$
M	545.33	421.19	577.38	765.11
T /K	296(2)	170(2)	123(2)	295(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/c$
Unit cell dimensions				
a /Å	9.401(4)	12.528(2)	15.736(2)	9.505(1)
b /Å	15.924(7)	5.414(6)	16.225(2)	18.215(2)
c /Å	16.360(7)	13.938(3)	10.768(2)	20.917(2)
α /°	90	90	90	90
β /°	104.78(1)	108.95(2)	103.95(2)	95.63(1)
γ /°	90	90	90	90
V /Å^3	2368.1(2)	894.1(2)	2668.2(7)	3604.0(6)
Z	4	2	4	4
$D_{calcd.}$ /g·cm^{-3}	1.530	1.565	1.437	1.410
μ /mm^{-1}	3.084	1.334	0.918	0.697
F(000)	1128	436	1200	1568
Crystal size /mm	0.10 × 0.10 × 0.10	0.44 × 0.18 × 0.10	0.51 × 0.28 × 0.25	0.20 × 0.20 × 0.10
Reflections collected	31168	7518	23795	7127
Unique reflections	3904 [R(int) = 0.0196]	2308 [R(int) = 0.0647]	6861 [R(int) = 0.0200]	6702 [R(int) = 0.0479]
Data/ restraints / parameters	3904 / 0 / 316	2308 / 2 / 123	6861 / 0 / 177	6702 / 1 / 379
Index ranges	$-10 \le h \le 10$ $-18 \le k \le 18$ $-18 \le l \le 19$	$-16 \le h \le 16$ $-7 \le k \le 7$ $-17 \le l \le 18$	$-26 \le h \le 26$ $-27 \le k \le 27$ $-18 \le l \le 17$	$0 \le h \le 11$ $0 \le k \le 22$ $-25 \le l \le 25$
Absorption correction (T_{min}, T_{max})	0.7479, 0.7689	0.31865, 1.00000	0.93887, 1.00000	0.8731, 0.9335
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0231, wR_2 = 0.0642	R_1 = 0.0545, wR_2 = 0.1356	R_1 = 0.0264, wR_2 = 0.0694	R_1 = 0.0520, wR_2 = 0.1219
R indices (all data)	R_1 = 0.0237, wR_2 = 0.0647	R_1 = 0.0676, wR_2 = 0.1559	R_1 = 0.0330, wR_2 = 0.0734	R_1 = 0.1226, wR_2 = 0.1657
Largest diff. peak and hole /e·Å^{-3}	0.275 and –0.212	1.522 and –0.966	0.502 and –0.265	0.781 and –0.552

48% occupancies (Figures S1–S5, Supporting Information). Both the occupancies and U_{iso} parameters were refined as free variables. Molecular graphics were used from PLATON[18a] and SCHAKAL.[18b] The crystallographic data and important bond parameters and various hydrogen bonds of complexes **1**–**4** are given in Table 1, Table 2, and Table 3, respectively.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-861021, -861022, -861023, and -861024 (**1**–**4**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Physical data of the ligands; Hydrogen bonding networks and packing diagrams for complexes **1**–**4**.

Results and Discussion

Syntheses and IR Spectroscopy

Scheme 1 depicts the formation of complexes with pyrrole based thiosemicarbazones, [$(C_4H_4N^4)(H)C^2{=}N^3{-}N^2(H){-}C^1(=S){-}N^1HR$; R = Ph, H_2L^1; Me, H_2L^2; H, H_2L^3]. The ligand H_2L^1 on reaction with $Ni(OAc)_2$ in methanol in 1:1 molar ratio was anticipated to act as N^4,N^3,S chelating ligand and yielded complexes of type, [Ni(κ^3-N^4,N^3,S-L^1)(D)] (D = py, PPh_3) on the pattern of salicylaldehyde thiosemicarbazones, which formed square-planar complexes, [Ni(O,N^3,S-L)(D)] (D = py, PPh_3).[19] However, H_2L^1 preferred the bis-square-planar complex, [Ni(κ^2-N^3, S-HL^1)$_2$] (**1**), involving deprotonation of only –N^2H– proton and no coordination by the co-ligand py/PPh_3 was observed. It is mentioned herein that the reactions of $Ni(OAc)_2$ with H_2L^2 or H_2L^3 in 1:2 molar ratio are known to yield similar types of complexes, [Ni(κ^2-N^3,S-HL^2)$_2$] and [Ni(κ^2-N^3,S-HL^3)$_2$.[8c] The reaction of $NiCl_2{\cdot}6H_2O$ with H_2L^2 in presence of triethylamine followed by addition of pyridine in acetonitrile did not yield the anticipated [Ni(κ^3-N^4,N^3,S-L^2)(py)] complex, moreover again a bis-square-planar complex, [Ni(κ^2-N^3,S-HL^2)$_2$] (**2**), similar to **1** has formed. However, in presence of bipyridine, the addition product, [Ni(κ^2-N^3,S-HL^2)$_2$(κ^2-N,N-bipy)] (**3**), was obtained. Thus, all the three ligands have shown preference for N^3,S chelation with pyrrole being pendant in the each case.

Furthermore, the reactions of $PdCl_2$(κ^2-P,P–PPh_2–CH_2–PPh_2) with H_2L^1 H_2L^2, and H_2L^3 in toluene in presence of triethylamine base were carried out. Herein, both halogen atoms were removed as $Et_3NH^+Cl^-$ salt and only the thio-ligand H_2L^3 gave a crystalline product of composition [Pd(κ^3-N^4,N^3,S-L^3)(κ^1-P–PPh_2–CH_2–P(O)Ph_2)] (**4**). The tricoordination by the thio ligand H_2L^3 is similar to that observed in

Zeitschrift für anorganische und allgemeine Chemie ZAAC Journal of Inorganic and General Chemistry

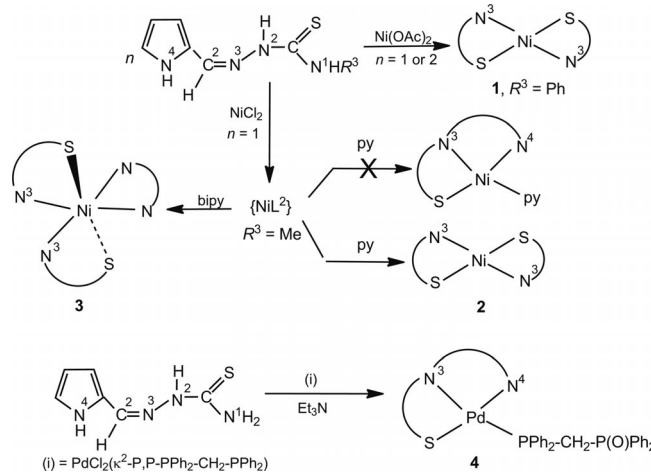
Table 2. Bond parameters of compounds **1**–**4**.

1			
Ni(1)–N(4)	1.913(1)	Ni(1)–N(8)	1.923(1)
Ni(1)–S(3)	2.179(7)	Ni(1)–S(2)	2.196(7)
N(4)–C(2)	1.308(2)	N(8)–C(14)	1.311(2)
C(1)–S(2)	1.742(2)	C(13)–S(3)	1.740(2)
N(4)–Ni(1)–S(3)	92.72(5)	N(8)–Ni(1)–S(2)	95.62(5)
N(8)–Ni(1)–S(3)	86.06(5)	N(4)–Ni(1)–S(2)	85.85(5)
N(4)–Ni(1)–N(8)	177.11(5)	S(3)–Ni(1)–S(2)	174.44(2)
2			
Ni(1)–N(3)	1.923(2)	S(1)–C(2)	1.730(3)
Ni(1)–S(1)	2.175(8)		
N(3)–Ni(1)–S(1)	85.76(7)	N(3)–Ni(1)–S(1)	94.24(7)
N(3)–Ni(1)–N(3)	180.00(1)	S(1)–Ni(1)–S(1)	180.00(3)
3			
Ni–N(1B)	2.085(7)	Ni–S$^{\#1}$	2.380(2)
S–C(6A)	1.739(7)		
N(1B)–Ni–N(1B)$^{\#1}$	78.45(4)	N(1B)–Ni–N(2A)$^{\#1}$	93.44(3)
N(2A)$^{\#1}$–Ni–N(2A)	97.06(3)	N(1B)–Ni–S	87.20(2)
N(1B)$^{\#1}$–Ni–S	94.24(2)	N(2A)$^{\#1}$–Ni–S	97.96(2)
N(1B)$^{\#1}$–Ni–N(2A)$^{\#1}$	165.02(3)	S–Ni–S$^{\#1}$	178.14(1)
4			
Pd–N1	2.064(6)	Pd–P1	2.247(2)
Pd–N2	2.008(5)	Pd–S1	2.266(2)
O1–P2	1.451(5)	C31–S1	1.764(7)
C25–P2	1.830(7)	C25–P1	1.844(7)
N2–Pd–N1	80.4(2)	N2–Pd–S1	83.22(2)
N2–Pd–P1	174.12(2)	N1–Pd–S1	163.59(2)
N1–Pd–P1	101.38(2)	P1–Pd–S1	95.02(7)

Table 3. Hydrogen bonds /Å for complexes **1**–**4**.

.	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
1	N(6)–H(6)···C(4)	0.860	2.835	3.467	131.75
	N(10)–H(10A)···C(16)	0.859	2.878	3.722	167.66
	N(10)–H(10A)···C(17)	0.859	2.588	3.419	162.85
	C(18)–H(18)···C(22)	0.930	2.831	3.656	148.35
	N(6)–H(6)···C(4)	0.860	2.835	3.467	131.75
	N(5) –H(5)···N(3)	0.859	2.218	2.712	116.35
2	N(4)–H(4N)···N(2)	0.857(2)	2.120(3)	2.681(3)	122.00
	N(1)–H(1N)···S(1)	0.853(2)	2.640(3)	3.411(3)	152.00
	C(3)–H(3A)···S(1)	0.950	2.400	3.046(3)	125.20
	C(7)–H(7A)···N(4)	0.950	2.590	3.456(4)	152.00
	C(7)–H(7A)···C(7)	0.950	2.732	3.615	154.95
	C(7)–H(7A)···C(4)	0.950	2.877	3.501	124.25
3	N(1A)–H(1A)···N(3A)	0.856(2)	2.164(2)	2.722(9)	122.60
	N(4A)–H(4A)···S$^{\#2}$	0.855(2)	2.619(2)	3.405(8)	153.30
	C(1A)–H(1AA)···C(5A)	0.950	2.795	3.652	150.62
	C(3B)–H(3BA)···S	0.951	2.826	3.670	148.52
4	C(21)–H(21)···C(3)	0.930	2.864	3.788	172.45
	N(4)–H(4B)···O(1)	0.861	2.056	2.789	142.62
	C(38)–H(38A)···C(11)	0.963	2.828	3.724	155.30
	C(36)–H(36)···C(26)	0.926	2.870	3.625	139.55
	C(35)–H(35)···C(5)	0.931	2.768	3.446	130.56

$[Pd(\kappa^3\text{-}N^4,N^3,S\text{-}L)(PPh_3)]$ complexes of pyrrole thiosemicarbazones reported earlier.[9] In absence of PPh_3, the pyrrole thiosemicarbazones are known to act as N^3,S-chelating ligands



Scheme 1.

forming bis square-planar complexes, $[Pd(\kappa^3\text{-}N^3,S\text{-}HL)_2]$.[8a,8c] In **4** the pendant $-PPh_2$ group involves auto oxidation to $-P(O)PPh_2$ during reaction. This behavior is unlike that observed in salicylaldehyde thiosemicarbazone complex, $[\{Pd(O,N^3,S\text{-}L)\}_2(\mu\text{-}P,P\text{–}PPh_2\text{–}CH_2\text{–}PPh_2)]$ having bridging diphopshine units.[20] The difference is attributed to the nature of the thioligand. The salicylaldehyde thiosemicarbazone forms $Pd(O,N^3,S\text{-}L)$ core with more electronegative oxygen as one of the donor atoms, which links to both ends of $PPh_2\text{–}CH_2\text{–}PPh_2$ forming bridged complex. On the other hand pyrrole thiosemicarbazone forms a $Pd(\kappa^3\text{-}N^4,N^3,S\text{-}L^3)$ core, which has less electronegative pyrrole nitrogen (N^4) as one of the donor atom instead of oxygen. The latter core appears to prefer to bind to only one $-PPh_2$ group of $PPh_2\text{–}CH_2\text{–}PPh_2$ and leaving the other pendant which undergoes oxidation to form $-P(O)Ph_2$.

The room temperature magnetic moment (μ_{eff}) of 2.98 BM suggested the presence of paramagnetic nickel atom in complex **3**. IR spectroscopic measurements revealed deprotonation of the $-N^2H-$ group in complexes **1**–**3**.[12] Complex **4** also involved deprotonation of $-N^4H-$ group during complex formation, which is further confirmed by single-crystal X-ray crystallography (vide infra). The diagnostic ν(C–S) bands (750–784 cm^{-1}) show low energy shifts compared to the free ligands (795–800 cm^{-1}), which suggest that the thio ligands are coordinating to the central metal atoms through the thiolato sulfur atom. The presence of phosphine in **4** is supported by its characteristic $\nu(P\text{–}C_{Ph})$ band at 1099 cm^{-1}.[21]

Crystal Structures

The crystal structure of complex, $[Ni(\kappa^2\text{-}N,S\text{-}HL^1)_2]$ (**1**), shows that two uni-negative thio ligands $(HL^1)^-$ are chelated to nickel(II) metal atom through azomethine nitrogen (N) and thiolato sulfur (S) atoms in *trans*-N_2S_2 manner forming five membered chelate rings (Figure 1). The bond lengths, Ni–N [1.913(1), 1.923(1) Å] and Ni–S [2.179(7), 2.196(7) Å], are similar to those in a related complex $[Ni(HL^3)_2]\cdot 2DMSO$ [Ni^{II}–N 1.910(3); Ni^{II}–S 2.177(1) Å].[8c] The C–S bond length

[1.742(2), 1.740(2) Å] shows a double bond character [C–S, 1.62; C=S 1.81 Å] as observed earlier for such thiosemicarbazone complexes.[9] Other bond parameters are similar to those reported in literature.[9] Trans angles, N–Ni–N [177.11(5)°] and S–Ni–S [174.44(2)°], suggest a slight deviation from regular square-planar arrangement. Complex [Ni(κ²-N,S-HL^2)$_2$] (**2**) has molecular structure and bond parameters similar to those of complex **1** (Figure 2).

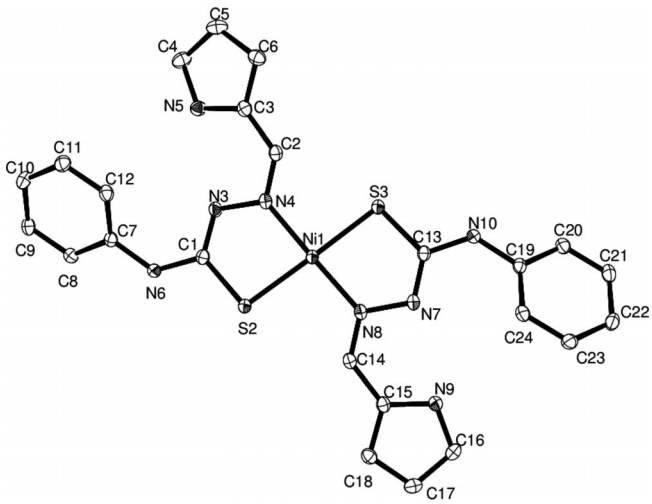


Figure 1. ORTEP diagram of complex [Ni(κ²-N,S-HL^1)$_2$] (**1**). Hydrogen atoms were omitted for clarity.

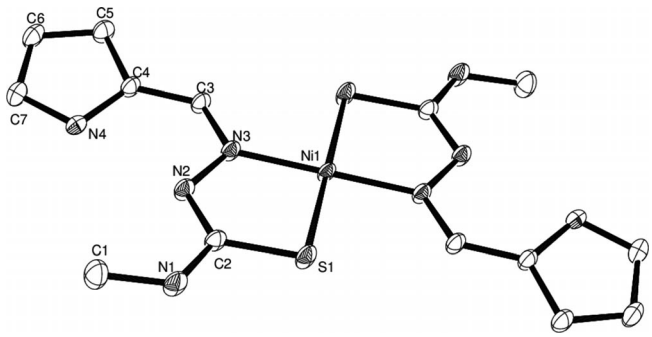


Figure 2. ORTEP diagram of complex [Ni(κ²-N,S-HL^2)$_2$] (**2**). Hydrogen atoms were omitted for clarity.

Complex [Ni(κ²-N,S-HL^2)$_2$(κ²-N,N-bipy)] (**3**) has four sites around the nickel atom occupied by N,S-donor atoms of two uni-negative $(HL^2)^-$ ligands and the remaining two sites are occupied by N,N-donor atoms of the bipyridine co-ligand (Figure 3). The trans bond angles, N–Ni–N, N–Ni–N, S–Ni–S are 165.02(3), 165.02(3), and 178.14(1)° respectively, and suggest distorted octahedral arrangement of the complex. The thiolato sulfur atoms are in *trans* position, whereas the azomethine nitrogen atoms and bipyridyl nitrogen atoms occupy the *cis* positions of the octahedron. The bond lengths, Ni–N [2.086(6) Å] and Ni–S [2.380(2) Å] are slightly longer than similar bond lengths found in square-planar complex **1** [Ni–N, 1.913(1), 1.923(1); Ni–S, 2.179(7), 2.196(7) Å], as expected. The nickel to bipyridine bond lengths, Ni–N_{bipy}, are 2.085(7), 2.085(7) Å, which are slightly longer than those of the nitrogen atoms of the thio ligand.

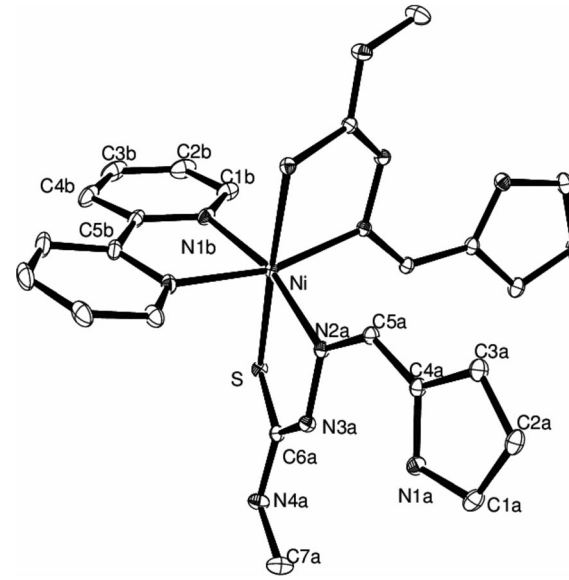


Figure 3. ORTEP diagram of complex [Ni(κ²-N,S-HL^2)$_2$(κ²-N,N-bipy)] (**3**). Hydrogen atoms were omitted for clarity.

The crystal structure of complex [Pd(κ³-N,N,S-L^3)(κ¹-P–PPh_2–CH_2–P(O)Ph_2)] (**4**) has shown that the dinegative thio ligand $(L^2)^{2-}$ is coordinated to the palladium(II) atom by N,N- and S-donor atoms. The fourth site around palladium is occupied by phosphorus atom of one PPh_2 group of dppm co-ligand, whereas the other end (PPh_2) undergoes aerial oxidation during reaction (Figure 4). The Pd–$N_{pyrrole}$ [2.064(6) Å], Pd–$N_{azomethine}$ [2.008(5) Å], Pd–S [2.266(2) Å] and Pd–P [2.2470 Å] distances are close to those of similar complex [PdL(PPh_3)] reported earlier.[9a] The trans angle, N(1)–Pd–S(1) [163.59(17)°] deviates significantly from linearity vis-à-vis the

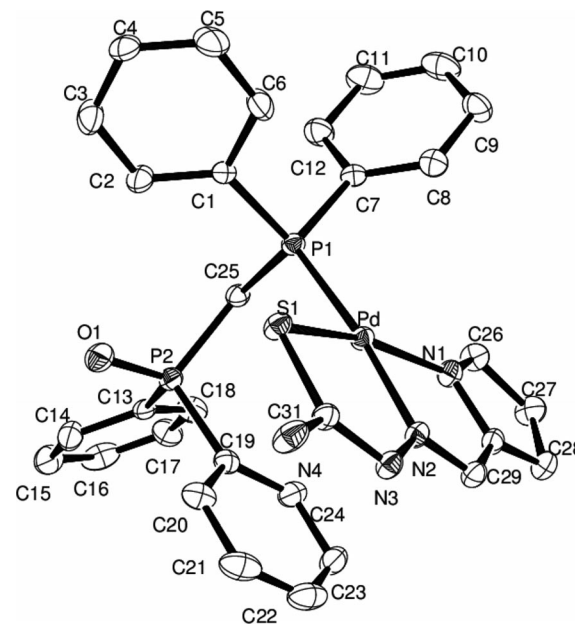


Figure 4. ORTEP diagram of complex [Pd(κ³-N,N,S-L^3)(κ¹-P–PPh_2–CH_2–P(O)Ph_2)] (**4**). The disordered toluene solvent molecule and hydrogen atoms were omitted for clarity.

Zeitschrift für anorganische und allgemeine Chemie ZAAC Journal of Inorganic and General Chemistry

second trans angle, N(2)–Pd–P(1) [174.12(17)°], probably due to strain in the five membered chelate rings. These bond angles suggest a distorted square-planar arrangement around the palladium(II) atom.

Solution Phase Behavior

The ^{1}H NMR spectrum of free thio ligand (H_2L^1) shows a signal at δ = 9.38 ppm, due to the hydrazinic N^2H hydrogen atoms. The absence of this signal in complex **1** confirms the deprotonation of N^2H hydrogen during complex formation.[9] Further, in this complex, the signals due to N^4H and N^1H protons are present at δ = 10.78, 6.63 ppm (H_2L^1: δ = 9.04 ppm). The C^2H signal appears as a singlet at δ = 7.41 ppm and is shifted upfield relative to the free ligand, δ = 7.71 ppm. The signals of the pyrrole ring protons appear at δ = 6.72 (C^6H), 6.53 (C^4H), and 6.17 (C^5H) ppm. Phenyl ring (N^1) protons are present as multiplet signals in the range δ = 7.36–7.26 ppm. Complex **2** displays a similar behavior (see Experimental Section). In this complex, the signal due to N^1H group is present at δ = 4.90 ppm and showed an upfield shift relative to the free ligand (δ = 8.06 ppm). Further, methyl hydrogen atoms (N^1) appear as doublet signal at δ = 2.98 ppm and showed an upfield shift relative to the free ligand (δ = 3.12 ppm).

In complex **4**, the signals of the N^2H and N^4H protons are absent, which suggests deprotonation during complexation.[9] Furthermore, there are two sets of *ortho* phenyl hydrogen atoms of the different phosphorus atoms of PPh_2–CH_2–PPh_2 one of these undergoes oxidation. The –CH_2– group of PPh_2–CH_2–PPh_2 ligand appears as triplet signal at δ = 3.50 ppm, due to coupling by adjacent phosphorus atoms. The ^{31}P NMR spectrum of complex **4** showed a coordination shift of 40.2 revealing coordination by the PPh_2 group. Another signal at –83.4 ppm was observed with a shift of 46.8 ppm relative to the free PPh_2–CH_2–PPh_2 ligand, which was assigned to the pendant –P(O)Ph_2 group. Complex **3** did not show any NMR signal, which confirmed the presence of paramagnetic nickel(II) atom. In this complex, the electronic absorption bands at 275 and 294–333 nm are assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively. The intense bands at 353, 374 nm are assigned to metal to ligand charge transfer transition (S→Ni). The other medium intensity bands at 413 nm are assigned to combined L→M (O→Ni) and ν_3 (d–d) transitions.[22]

Conclusions

Pyrrole-2-carbaldehyde thiosemicarbazones with nickel(II) showed coordination mode III (bi-coordination) in complexes **1**–**3**; unlikely, the Pd^{II} complex **4** favored coordination mode V (tri-coordination). It could be attributed to the higher flexibility of the Ni^{II} binding to the pyrrole nitrogen atom (Ni-κ^1-N^4-$C_4H_4N^4$), the corresponding Pd-κ^1-N^4-$C_4H_4N^4$ bond in **4** is more rigid. Further, PPh_2–CH_2–PPh_2 showed autooxidation of pendant –PPh_2 moiety. This behavior is unlikely to that observed in the salicylaldehyde thiosemicarbazone complex [{Pd(κ^3-O,N^3,S-L)}$_2$(μ-P,P-PPh_2–CH_2–PPh_2)] with a bridging diphosphine ligand.[20]

Acknowledgement

Financial assistance from *Council of Scientific and Industrial Research (CSIR)* (letter no. 09/254(0188)/2009-EMR-I), New Delhi is gratefully acknowledged.

References

[1] a) D. X. West, S. Padhye, P. B. Sonawane, *Struct. Bonding (Berlin)* **1991**, *76*, 4; b) S. Padhye, G. B. Kauffman, *Coord. Chem. Rev.* **1985**, *63*, 127; c) D. X. West, A. E. Liberta, S. B. Padhye, R. C. Chikate, P. B. Sonawane, A. S. Kumbhar, R. G. Yerande, *Coord. Chem. Rev.* **1993**, *123*, 49; d) J. S. Casas, M. S. Garcia-Tasende, J. Sordo, *Coord. Chem. Rev.* **2000**, *209*, 197.

[2] a) D. Kovala-Demertzi, M. A. Demertzis, V. Varagi, A. Papageorgiou, D. Mourelatos, E. Mioglou, Z. Lakovidou, A. Kotsis, *Chemotherapy* **1998**, *44*, 421; b) D. Kovala-Demertzi, J. R. Miller, N. Kourkoumelis, S. K. Hadjikakou, M. A. Demertzis, *Polyhedron* **1999**, *18*, 1005; c) D. Kovala-Demertzi, M. A. Demertzis, A. Castineiras, D. X. West, *Polyhedron* **1998**, *17*, 3739.

[3] A. G. Quiroga, J. M. Perez, I. Lopez-Solera, J. R. Masaguer, A. Luque, P. Roman, A. Edwards, C. Alonso, C. Navarro-Ranninger, *J. Med. Chem.* **1998**, *41*, 1399.

[4] a) M. Maji, S. Ghosh, S. K. Chattopadhyay, T. C. W. Mak, *Inorg. Chem.* **1997**, *36*, 2938; b) L. J. Ashfield, A. R. Cowley, J. R. Dilworth, P. S. Donnelly, *Inorg. Chem.* **2004**, *43*, 4121; c) . A. R. Cowley, J. R. Dilworth, P. S. Donnelly, E. Labisbal, A. Sousa, *J. Am. Chem. Soc.* **2002**, *124*, 5270; d) T. S. Lobana, S. Khanna, R. J. Butcher, A. D. Hunter, M. Zeller, *Inorg. Chem.* **2007**, *46*, 5826.

[5] T. S. Lobana, R. Sharma, G. Bawa, S. Khanna, *Coord. Chem. Rev.* **2009**, *253*, 977.

[6] a) R. K. Mahajan, T. P. S. Walia, Sumanjit, T. S. Lobana, *Anal. Sci.* **2006**, *22*, 389; b) R. K. Mahajan, I. Kaur, T. S. Lobana, *Talanta* **2003**, *59*,101; c) R. K. Mahajan, T. P. S. Walia, Sumanjit, T. S. Lobana, *Talanta* **2005**, *67*, 755; d) R. K. Mahajan, R. Kaur, T. S. Lobana, *Ind. J. Chem. A* **2006**, *45*, 639.

[7] a) T. S. Lobana, Rekha, R. J. Butcher, *Transition Met. Chem.* **2004**, *29*, 291; b) T. S. Lobana, Rekha, R. J. Butcher, A. Castineiras, E. Bermejo, P. V. Bharatam, *Inorg. Chem.* **2006**, *45*, 1535; c) T. S. Lobana, S. Khanna, R. Sharma, G. Hundal, R. Sultana, M. Chaudhary, R. J. Butcher, A. Castineiras, *Cryst. Growth Des.* **2008**, *8*, 1203; d) R. Carballo, A. Castineiras, T. Perez, *Z. Naturforsch.* **2001**, *56b*, 881; e) E. Bermejo, A. Castineiras, T. Perez, R. Carballo, W. Hiller, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2377; f) A. Castineiras, R. Carballo, T. Perez, *Polyhedron* **2001**, *20*, 441; g) Y.-P. Tian, C.-Y. Duan, C.-Y. Zhao, X.-Z. You, T. C. W. Mak, Z.-Y. Zhang, *Inorg. Chem.* **1997**, *36*, 1247.

[8] a) R. Alonso, E. Bermejo, R. Carballo, A. Castineiras, T. Perez, *Z. Naturforsch.* **2001**, *56b*, 219; b) T. S. Lobana, A. Sanchez, J. S. Casas, A. Castineiras, J. Sordo, M. S. Garcia-Tasende, E. M. Vazquez-Lopez, *J. Chem. Soc. Dalton Trans.* **1997**, 4289; c) R. Alonso, E. Bermejo, A. Castineiras, T. Perez, R. Carballo, *Z. Anorg. Allg. Chem.* **1997**, *623*, 818; d) U. Abram, K. Ortner, R. Gust, K. Sommer, *J. Chem. Soc. Dalton Trans.* **2000**, 735.

[9] a) T. S. Lobana, G. Bawa, A. Castineiras, R. J. Butcher, *Inorg. Chem. Commun.* **2007**, *10*, 505; b) T. S. Lobana, P. Kumari, R. J. Butcher, T. Akitsu, Y. Aritake, J. Perles, F. J. Fernandez, M. C. Vega, *J. Organomet. Chem.* **2012**, *701*, 17.

[10] T. S. Lobana, A. Sánchez, J. S. Casas, A. Castiñeíras, J. Sordo, M. S. García-Tasende, E. M. Vázquez-López, *J. Chem. Soc. Dalton Trans.* **1997**, 4289.

[11] G. M. Sheldrick, *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, **1997**.

[12] Oxford Diffraction, *CrysAlisPro CCD* and *CrysAlisPro RED*, Oxford Diffraction Ltd. Yarnton, UK, **2009**.

[13] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr. Sect. A* **1968**, *24*, 351.
[14] G. M. Sheldrick, *SHELXTL-PC*, release 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, **1995**.
[15] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, SIR-92, *J. Appl. Crystallogr.* **1993**, *26*, 343.
[16] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.
[17] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.
[18] a) . A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7; b) *SCHAKAL-97*, A Computer Program for the Graphic Representation of Molecular and Crystallographic Models, University of Freiburg i. Br., Germany, **1997**.
[19] T. S. Lobana, P. Kumari, G. Hundal, R. J. Butcher, *Polyhedron* **2010**, *29*, 1130.
[20] T. S. Lobana, G. Bawa, G. Hundal, R. J. Butcher, A. Castineiras, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1447.
[21] a) T. S. Lobana, G. Bawa, G. Hundal, M. Zeller, *Z. Anorg. Allg. Chem.* **2008**, *634*, 931; b) T. S. Lobana, P. Kumari, M. Zeller, R. J. Butcher, *Inorg. Chem. Commun.* **2008**, *11*, 972; c) T. S. Lobana, P. Kumari, R. Sharma, A. Castineiras, R. J. Butcher, T. Akitsu, Y. Aritake, *Dalton Trans.* **2011**, *40*, 3219.
[22] a) J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., Harper Collins, New York, **1993**; b) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, New York, **1984**.

Received: January 12, 2012
Published Online: March 25, 2012

