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Synthesis, characterization, structure, redox property, antibacterial and catalytic activity of tridentate Schiff base cobalt(III), nickel(II) and palladium(II) complexes

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ABSTRACT

Ligand, HL, 2-((2-(benzylthio)phenylimino)methyl)phenol, upon reaction with Co(NO₃)₃·6H₂O, Ni(OAc)₂₋ -4H₂O and PdCl₂ separately afforded complexes [(L)₂Co]NO₃(1), [(L)₂Ni](2) and [(L)PdCl](3) respectively. The new complexes were characterized by usual spectroscopic studies like UV-Vis, IR and NMR and authenticated by X-ray structure determination on [(L)₂Co]NO₃, [(L)₂Ni]. The analysis of crystal structures revealed that in all the complexes the ligand HL binds the metal center as uni-negative anion; L⁻ dissociating phenolic proton and offers (O, N, S) tridentate binding mode to the metal. The compound [Co(L)₂]-NO₃ is tested for *in vitro* antibacterial activity. Complex **3**, acts as a catalyst in Heck reaction for a number of substrates. Complexes 1 and 2 exhibited a quasi reversible oxidative responses at 0.97 and 0.85 V, respectively, versus SCE. The electronic spectra and redox properties of the complexes have been explained with DFT computation.

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1. Introduction

Metal complexes incorporating ONS donor Schiff base ligands where the ligands containing phenolic OH, the azomethine group and thioether sulfur are scarce [1]. The Schiff bases are easily synthesized and form complexes with almost all metal ions. There have been many reports on activity of Schiff base complexes in homogeneous and heterogeneous catalysis [2-10]. The carboncarbon bond forming reactions (Suzuki and Heck) is an important and reliable tool in organic synthesis [11–18]. The Heck coupling of an aryl halide with olefins is renowned as the most successful method for forming a carbon-carbon bond in the synthesis of natural products, biologically active molecules [19-28] where the recovery of the palladium catalyst is a challenging task [29-31]. Several strategies reported in the literature include a high catalyst loading, higher temperature and relatively longer reaction time as well as the participation of bases, ligands and metal salts additives. So, the more mild, convenient and efficient catalytic system should

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(J.L. Pratihar).

still be developed. Furthermore, Schiff base complexes are very much important for their interesting applications in biological, clinical, and pharmacological areas including antibacterial, antifungal, and anticancer [32-43]. Notable examples of the ligand systems are thiosemicarbazone, semicarbazone and related ligands which grab our attention due to their activity against influenza, protozoa, smallpox and viral diseases [32-43]. Our present communication focuses on catalytic activity, redox behavior and antibacterial property of cobalt(III), nickel(II) and palladium(II) complexes of ONS donor Schiff base ligand.

Herein we report the reactions of tridentate 2-((2-(benzylthio)phenylimino)methyl)phenol, HL, ligand with Co(NO₃)₃·6H₂O, Ni(OAc)₂·4H₂O and PdCl₂ separately to form complexes of composition [(L)₂Co]NO₃, 1, [(L)₂Ni], 2 and [(L)PdCl], 3, respectively where, the ligand offers (O, N, S) binding mode to the metal. The complex formations have been authenticated on the basis of Xray studies and ¹H NMR spectroscopy. Antibacterial activity of [(L)₂Co]NO₃ complex have been studied against some bacteria. Heck coupling reactions were carried out, in presence of air and moisture, using [(L)PdCl] as catalysts. The redox property of the complexes has been studied electrochemically. Plausible descriptions of redox orbitals and electronic spectra have been ascribed on the basis of single point DFT calculations.



Collaborator for experiment related to antibacterial activity.

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2. Experimental

2.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by reported procedure [44]. Cobalt nitrate hexahydrate, nickel acetate tetrahydrate, palladium chloride, benzyl chloride and salicylaldehyde were purchased from Emark, India. 2-Aminothiophenol was purchased from Aldrich. 2-(benzylthio)aniline and 2-((2-(benzylthio)phenylimino)methyl)phenol was prepared following the reported procedures [1,45]. Iodobenzene, bromobenzene, 1-iodo-3,5-dimethylbenzene, 1-iodo-3,4-dimethylbenzene, 1-iodo-2-nitrobenzene, 1-bromo-3,5-dimethylbenzene, 1-bromo-2-nitrobenzene, styrene were purchased from Aldrich.

2.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin-Elmer 2400 C, H, N, S/O series II elemental analyzer. Infrared spectra were recorded on a Parkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. ¹H NMR spectra were obtained on Bruker 400 NMR spectrometers in CDCl₃ using TMS as the internal standard. Electrochemical measurements were made under dinitrogen atmosphere using a CH instruments model 600D potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

2.3. DFT calculations

Using the X-ray coordinates of the $[(L)_2Co]^+$ and $[(L)_2Ni]$ complexes, ground state electronic structure calculations have been carried out using DFT [47] methods with the Orca 2.7 program [46]. Becke's hybrid function [47] with the Lee–Yang–Parr (LYP) correlation function [48] was used throughout the study. LANL2DZ valence and effective core potential functions were used. All energy calculations were performed using the self-consistent field "tight" option of the Orca 2.7 program to ensure sufficiently well converged values for the state energies.

2.4. Syntheses of complexes [(L)₂Co]NO₃, [(L)₂Ni] and [(L)PdCl]

2.4.1. [(L)₂Co]NO₃

Cobalt nitrate hexahydrate (1 mmol, 291 mg) was mixed with the methanolic solution of the Schiff bases (2 mmol 756 mg). The color of the solution changes from pink to redish brown. The resulting solution was stirred in presence of slight heat for 4 h. Total solution was kept for crystallization. After few days single crystal was obtained. Yield: 60%. *Anal.* Calc. for $C_{40}H_{32}N_3O_5S_2Co$ (757.76): C, 63.34; H, 4.22; N, 5.54. Found: C, 63.21; H, 4.29; N, 5.36%. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 445 (1560), 345 (17300), 270 (35470), 240 (35980). IR (KBr pellets, cm⁻¹): v = 1605 (CH=N), 1529 (C–O), 1337(NO₃), 756 (C–S). ¹H NMR CDCl₃: δ 7.94 (s, 1H), 7.56 (d, 2H), 7.30–7.23 (m, 3H), 7.16 (t, 1H), 7.02–6.96 (m, 3H), 6.76 (d, 2H), 6.57 (t, 2H), 3.71–3.66 (m, 2H). $E_{1/2}$ [V]: 0.97.

2.4.2. $[(L)_2Ni]$

Nickel acetate tetrahydrate (1 mmol, 250 mg) was mixed with the methanolic solution of the Schiff bases (2 mmol 756 mg). The color of the solution changes from green to olive green. The resulting solution was refluxed for 6 h and filtered. Total solution was kept for crystallization. After few days single crystal was obtained, these are collected by filtration and washed with MeOH. Yield: 70%. *Anal.* Calc. for C₄₀H₃₂N₂O₂S₂Ni (695.5): C, 69.01; H, 4.63; N, 4.02. Found: C, 69.36; H, 4.32; N, 3.87%. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ cm⁻¹) = 460 (1950), 325 (4120), 250 (11130). IR (KBr pellets, cm⁻¹): v = 1604 (CH=N), 1523 (C–O), 752 (C–S). $E_{1/2}$ [V]: 0.85.

2.4.3. [(L)PdCl]

PdCl₂ (0.065 g, 0.368 mmol) was dissolved by refluxing in 20 ml acetonitrile, an orange color solution resulted. To this solution HL (0.092 g, 0.370 mmol) in acetonitrile (10 ml) was added. The color of the solution changes from light orange to brown. The mixture was refluxed for 3 h. Total solution was kept for crystallization. After few days single crystal was obtained, these are collected by filtration and washed with acetonitrile. Yield: 80%. *Anal.* Calc. for C₂₀H₁₆NOSCIPd (460.31): C, 52.18; H, 3.50; N, 3.05. Found: C, 52.35; H, 3.24; N, 3.18%. UV–Vis spectrum (CH₂Cl₂) λ_{max} (ε , M⁻¹ - cm⁻¹) = 455 (3070), 305 (4650), 255 (9000). IR (KBr pellets, cm⁻¹): ν = 1606 (CH=N), 1523 (C–O), 758 (C–S). ¹H NMR CDCl₃: δ 8.23 (s, 1H), 7.66–7.21 (m, 12H), 6.64 (d, 1H), 4.49 (d, 1H), 4.33 (d, 1H).

2.5. Antibacterial activity

2.5.1. Microorganisms

The microorganisms used in this study included *Escherichia coli* DH5, *Bacillus subtilis* ATCC6623 and *Staphylococcus* ATCC25923. These strains were kindly provided by Prof. Prasanta Kr. Bag, Department of Biochemistry, University of Calcutta, Kolkata, West Bengal, India.

2.5.2. Drug solution

The compound of cobalt $[(L)_2Co]NO_3$ (7 mg) was screened for its antibacterial activity. For this drug was dissolved in 700 μ l of 100% DMSO to get the concentration of 1 mg/ml, which was used as stock solution. Evaluation of the activity was carried out by broth dilution technique using Mueller Hinton medium.

2.5.3. Preparation of inoculum

An inoculum of the microorganism was prepared from 4 h MBH (Mueller Hinton Broth) cultures and suspensions were adjusted with a turbidity equivalent to that of a 0.5 McFarland standard. 50×10^6 CFU/ml were inoculated in each bacterial culture tube.

2.5.4. Determination of minimum inhibitory concentration (MIC) and determination of minimal bactericidal concentration (MBC)

MIC and MBC of the cobalt compound was assessed using the broth microdilution method recommended by the National Committee of Clinical Laboratory Standards [49]. The bacterial culture tubes were prepared by dispensing 10 μ l of the inoculated broth into each tube. A 25 μ l aliquot of the cobalt compound was added. The concentration of the cobalt compound tested were 2, 20, 32, 80, 100, 128, 200 μ g/ml. Dilutions of Tetracycline served as positive control while broth with 25 μ l of 100% DMSO was used as a negative control tubes were covered and incubated for 24 h in ambient air at 37 °C. After incubation MIC were read visually following a reported method [50]. All the contents of the test tubes were plated to nutrient agar (Hi-Media) and incubated. The minimum bactericidal concentration (MBC) was defined as a 99.9% reduction in CFU from the starting inoculum after 24 h incubation interval.

Table 1					
Crystallographic	data	for	1	and	2.

$\begin{array}{llllllllllllllllllllllllllllllllllll$			
NO3H20Formula weight757.76713.51Crystal systemmonoclinicmonoclinicSpace group $P 21/c$ $P 21/c$ a (Å)18.0644(3)12.7395(3) b (Å)10.1594(1)30.6303(7) c (Å)20.7710(3)17.6227(4) α (°)9090 β (°)113.2730(10)103.6870(10) γ (°)9090 λ (Å)0.710730.71073 V (Å ³)3501.80(9)6681.4(3) $F(000)$ 15682960 Z 44 T (K)295296 D (mg/m ⁻³)1.4371.415 μ (mm ⁻¹)0.6600.749 θ Min-Max (°)2.0, 28.31.4, 29.3Reflections measured31888104860Unique reflections (R_{int})8652 (0.051)18005 (0.044)No. of reflections used55711940 $[I > 2\sigma(I)]$ 0.04440.0423 wR_2 (all data)0.11970.1445Goodness-of-fit (GOF) on F^2 1.020.80	Chemical formula	$C_{40}H_{32}N_2O_2S_2Co$,	$C_{40}H_{32}N_2O_2S_2Ni$,
Formula weight757.76713.51Crystal systemmonoclinicmonoclinicSpace group $P 21/c$ $P 21/c$ a (Å)18.0644(3)12.7395(3) b (Å)10.1594(1)30.6303(7) c (Å)20.7710(3)17.6227(4) α (°)9090 β (°)113.2730(10)103.6870(10) γ (°)9090 β (°)113.2730(10)103.6870(10) γ (°)9090 λ (Å)0.710730.71073 V (Å ³)3501.80(9)6681.4(3) $F(000)$ 15682960 Z 44 T (K)295296 D (mg/m ⁻³)1.4371.415 μ (mm ⁻¹)0.6600.749 θ Min-Max (°)2.0, 28.31.4, 29.3Reflections measured31888104860Unique reflections (R_{int})8652 (0.051)18005 (0.044)No. of reflections used557711940 $[I > 2\sigma(I)]$ 0.04440.0423 wR_2 (all data)0.11970.1445Goodness-of-fit (GOF) on F^2 1.020.80		NO ₃	H ₂ O
Crystal systemmonoclinicmonoclinicSpace group $P 21/c$ $P 21/c$ a (Å)18.0644(3)12.7395(3) b (Å)10.1594(1)30.6303(7) c (Å)20.7710(3)17.6227(4) α (°)9090 β (°)113.2730(10)103.6870(10) γ (°)9090 β (°)113.2730(10)103.6870(10) γ (°)9090 λ (Å)0.710730.71073 V (Å ³)3501.80(9)6681.4(3) $F(000)$ 15682960 Z 44 T (K)295296 D (mg/m ⁻³)1.4371.415 μ (mm ⁻¹)0.6600.749 ϕ Min-Max (°)2.0, 28.31.4, 29.3Reflections measured31888104860Unique reflections (R_{int})8652 (0.051)18005 (0.044)No. of reflections used555711940 $[I > 2\sigma(I)]$ 0.04440.0423 wR_2 (all data)0.11970.1445Goodness-of-fit (GOF) on F^2 1.020.80	Formula weight	757.76	713.51
Space group $P 21/c$ $P 21/c$ a (Å) 18.0644(3) 12.7395(3) b (Å) 10.1594(1) 30.6303(7) c (Å) 20.7710(3) 17.6227(4) α (°) 90 90 β (°) 113.2730(10) 103.6870(10) γ (°) 90 90 γ (°) 90 90 λ (Å) 0.71073 0.71073 V (Å ³) 3501.80(9) 6681.4(3) $F(000)$ 1568 2960 Z 4 4 T (K) 295 296 D (mg/m ⁻³) 1.437 1.415 μ (mm ⁻¹) 0.660 0.749 θ Min–Max (°) 2.0, 28.3 1.4, 29.3 Reflections measured 31888 104860 Unique reflections (R_{int}) 8652 (0.051) 18005 (0.044) No. of reflections used 5557 11940 $[I > 2\sigma(I)]$ 0.0444 0.0423 wR_2 (all data) 0.1197 0.1445	Crystal system	monoclinic	monoclinic
a (Å)18.0644(3)12.7395(3)b (Å)10.1594(1)30.6303(7)c (Å)20.7710(3)17.6227(4) α (°)9090 β (°)113.2730(10)103.6870(10) γ (°)9090 λ (Å)0.710730.71073V (Å3)3501.80(9)6681.4(3)F(000)15682960Z44T (K)295296D (mg/m ⁻³)1.4371.415 μ (mm ⁻¹)0.6600.749 θ Min-Max (°)2.0, 28.31.4, 29.3Reflections measured31888104860Unique reflections (R_{int})8652 (0.051)18005 (0.044)No. of reflections used55711940 $[I > 2\sigma(I)]$ 0.04440.0423wR2 (all data)0.11970.1445Goodness-of-fit (GOF) on F^2 1.020.80	Space group	P 21/c	P 21/c
$\begin{array}{lll} b(\dot{A}) & 10.1594(1) & 30.6303(7) \\ c(\dot{A}) & 20.7710(3) & 17.6227(4) \\ \alpha(^{\circ}) & 90 & 90 \\ \beta(^{\circ}) & 113.2730(10) & 103.6870(10) \\ \gamma(^{\circ}) & 90 & 90 \\ \dot{\lambda}(\dot{A}) & 0.71073 & 0.71073 \\ V(\dot{A}^3) & 3501.80(9) & 6681.4(3) \\ F(000) & 1568 & 2960 \\ Z & 4 & 4 \\ T(K) & 295 & 296 \\ D(mg/m^{-3}) & 1.437 & 1.415 \\ \mu(mm^{-1}) & 0.660 & 0.749 \\ \theta \operatorname{Min-Max}(^{\circ}) & 2.0, 28.3 & 1.4, 29.3 \\ \operatorname{Reflections} measured & 31888 & 104860 \\ Unique reflections (R_{int}) & 8652 (0.051) & 18005 (0.044) \\ \operatorname{No. of reflections used } 557 & 11940 \\ [I > 2\sigma(I)] & \\ R_1 [I > 2\sigma(I)] & 0.0444 & 0.0423 \\ wR_2 (all data) & 0.1197 & 0.1445 \\ \operatorname{Goodness-of-fit}(GOF) on F^2 & 1.02 & 0.80 \\ \end{array}$	a (Å)	18.0644(3)	12.7395(3)
$\begin{array}{cccc} (\dot{A}) & 20.7710(3) & 17.6227(4) \\ \alpha(^{\circ}) & 90 & 90 \\ \beta(^{\circ}) & 113.2730(10) & 103.6870(10) \\ \gamma(^{\circ}) & 90 & 90 \\ \dot{\lambda}(\dot{A}) & 0.71073 & 0.71073 \\ V(\dot{A}^3) & 3501.80(9) & 6681.4(3) \\ F(000) & 1568 & 2960 \\ Z & 4 & 4 \\ T(K) & 295 & 296 \\ D(mg/m^{-3}) & 1.437 & 1.415 \\ \mu(mm^{-1}) & 0.660 & 0.749 \\ \theta & Min-Max(^{\circ}) & 2.0, 28.3 & 1.4, 29.3 \\ Reflections measured & 31888 & 104860 \\ Unique reflections (R_{int}) & 8652 (0.051) & 18005 (0.044) \\ No. of reflections used & 5557 & 11940 \\ [I > 2\sigma(I)] & \\ R_1 [I > 2\sigma(I)] & 0.0444 & 0.0423 \\ wR_2 (all data) & 0.1197 & 0.1445 \\ Goodness-of-fit (GOF) on F^2 & 1.02 & 0.80 \\ \end{array}$	b (Å)	10.1594(1)	30.6303(7)
$\begin{array}{ccccc} \alpha \left(^{\circ} \right) & 90 & 90 \\ \beta \left(^{\circ} \right) & 113.2730(10) & 103.6870(10) \\ \gamma \left(^{\circ} \right) & 90 & 90 \\ \lambda \left(A \right) & 0.71073 & 0.71073 \\ V \left(A^3 \right) & 0.71073 & 0.71073 \\ V \left(A^3 \right) & 3501.80(9) & 6681.4(3) \\ F(000) & 1568 & 2960 \\ Z & 4 & 4 \\ T \left(K \right) & 295 & 296 \\ D \left(mg/m^{-3} \right) & 1.437 & 1.415 \\ \mu \left(mm^{-1} \right) & 0.660 & 0.749 \\ \theta \operatorname{Min-Max} \left(^{\circ} \right) & 2.0, 28.3 & 1.4, 29.3 \\ \text{Reflections measured} & 31888 & 104860 \\ \text{Unique reflections (R_{int})} & 8652 \left(0.051 \right) & 18005 \left(0.044 \right) \\ \text{No. of reflections used} & 5557 & 11940 \\ \left[I > 2\sigma(I) \right] & I197 & 0.1445 \\ \mathbf{K}_1 \left[I > 2\sigma(I) \right] & 0.0444 & 0.0423 \\ \mathbf{w}_2 \left(\text{all data} \right) & 0.1197 & 0.1445 \\ \text{Goodness-of-fit (GOF) on } F^2 & 1.02 & 0.80 \\ \end{array}$	<i>c</i> (Å)	20.7710(3)	17.6227(4)
$\begin{array}{lll} \beta \left(^{\circ} \right) & 113.2730(10) & 103.6870(10) \\ \gamma \left(^{\circ} \right) & 90 & 90 \\ \lambda \left(^{A} \right) & 0.71073 & 0.71073 \\ V \left(^{A} \right) & 3501.80(9) & 6681.4(3) \\ F(000) & 1568 & 2960 \\ Z & 4 & 4 \\ T \left(K \right) & 295 & 296 \\ D \left(mg/m^{-3} \right) & 1.437 & 1.415 \\ \mu \left(mm^{-1} \right) & 0.660 & 0.749 \\ \theta \ Min-Max \left(^{\circ} \right) & 2.0, 28.3 & 1.4, 29.3 \\ Reflections measured & 31888 & 104860 \\ Unique reflections (R_{int}) & 8652 (0.051) & 18005 (0.044) \\ No. of reflections used & 5557 & 11940 \\ \left[I > 2 \sigma(I) \right] & 0.0444 & 0.0423 \\ WR_2 \left(all \ daa \right) & 0.1197 & 0.1445 \\ Goodness-of-fit (GOF) on F^2 & 1.02 & 0.80 \\ \end{array}$	α (°)	90	90
$\begin{array}{llllllllllllllllllllllllllllllllllll$	β (°)	113.2730(10)	103.6870(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	γ (°)	90	90
$\begin{array}{lll} V({\rm \AA}^3) & 3501.80(9) & 6681.4(3) \\ F(000) & 1568 & 2960 \\ Z & 4 & 4 \\ T({\rm K}) & 295 & 296 \\ D({\rm mg/m}^{-3}) & 1.437 & 1.415 \\ \mu({\rm mm}^{-1}) & 0.660 & 0.749 \\ \theta{\rm Min-Max}(^\circ) & 2.0, 28.3 & 1.4, 29.3 \\ {\rm Reflections\ measured} & 31888 & 104860 \\ Unique\ reflections(R_{\rm int}) & 8652(0.051) & 18005(0.044) \\ {\rm No.\ of\ reflections\ used} & 557 & 11940 \\ \hline [I \geq 2\sigma(I)] & I1220(I) \\ R_1[I \geq 2\sigma(I)] & 0.0444 & 0.0423 \\ wR_2({\rm all\ dat}) & 0.1197 & 0.1445 \\ {\rm Goodness-of\ -fit\ (GOF)\ on\ F^2} & 1.02 & 0.80 \\ \end{array}$	λ (Å)	0.71073	0.71073
$\begin{array}{llllllllllllllllllllllllllllllllllll$	V (Å ³)	3501.80(9)	6681.4(3)
Z44 $T(K)$ 295296 $D (mg/m^{-3})$ 1.4371.415 $\mu (mm^{-1})$ 0.6600.749 θ Min-Max (°)2.0, 28.31.4, 29.3Reflections measured31888104860Unique reflections (R_{int})8652 (0.051)18005 (0.044)No. of reflections used557711940 $[I > 2\sigma(I)]$ 0.04440.0423 wR_2 (all data)0.11970.1445Goodness-of-fit (GOF) on F^2 1.020.80	F(000)	1568	2960
T (K)295296 D (mg/m^{-3})1.4371.415 μ (mm^{-1})0.6600.749 θ Min-Max (°)2.0, 28.31.4, 29.3Reflections measured31888104860Unique reflections (R_{int})8652 (0.051)18005 (0.044)No. of reflections used557711940 $[I > 2\sigma(I)]$ 0.04440.0423 wR_2 (all data)0.11970.1445Goodness-of-fit (GOF) on F^2 1.020.80	Ζ	4	4
$\begin{array}{llllllllllllllllllllllllllllllllllll$	T (K)	295	296
$\begin{array}{lll} \mu \ (mm^{-1}) & 0.660 & 0.749 \\ \theta \ Min-Max \ (^{\circ}) & 2.0, 28.3 & 1.4, 29.3 \\ Reflections measured & 31888 & 104860 \\ Unique reflections (R_{int}) & 8652 \ (0.051) & 18005 \ (0.044) \\ No. of reflections used & 5557 & 11940 \\ \hline [l > 2\sigma(l)] & 0.0444 & 0.0423 \\ wR_2 \ (all \ data) & 0.1197 & 0.1445 \\ Goodness-of-fit \ (GOF) \ on \ F^2 & 1.02 & 0.80 \\ \end{array}$	$D (mg/m^{-3})$	1.437	1.415
$\begin{array}{llllllllllllllllllllllllllllllllllll$	μ (mm ⁻¹)	0.660	0.749
Reflections measured 31888 104860 Unique reflections (R_{int}) 8652 (0.051) 18005 (0.044) No. of reflections used 5557 11940 $[I > 2\sigma(I)]$ R_1 [$I > 2\sigma(I)$] 0.0444 0.0423 wR ₂ (all data) 0.1197 0.1445 0.040 Goodness-of-fit (GOF) on F^2 1.02 0.80 0.02	θ Min-Max (°)	2.0, 28.3	1.4, 29.3
Unique reflections (R_{int})8652 (0.051)18005 (0.044)No. of reflections used555711940 $[I > 2\sigma(I)]$ 0.04440.0423 wR_2 (all data)0.11970.1445Goodness-of-fit (GOF) on F^2 1.020.80	Reflections measured	31888	104860
No. of reflections used555711940 $[I > 2\sigma(I)]$ R_1 $I > 2\sigma(I)$ 0.0423 w_{R_2} (all data)0.11970.1445Goodness-of-fit (GOF) on F^2 1.020.80	Unique reflections (R _{int})	8652 (0.051)	18005 (0.044)
$ \begin{array}{c} [I > 2\sigma(I)] \\ R_1 \ [I > 2\sigma(I)] \\ wR_2 \ (all \ data) \\ Goodness-of-fit \ (GOF) \ on \ F^2 \\ \end{array} \begin{array}{c} 0.0444 \\ 0.1197 \\ 1.02 \\ 0.80 \end{array} \begin{array}{c} 0.0423 \\ 0.1445 \\ 0.80 \end{array} $	No. of reflections used	5557	11940
$R_1 [I > 2\sigma(I)]$ 0.0444 0.0423 wR_2 (all data) 0.1197 0.1445 Goodness-of-fit (GOF) on F^2 1.02 0.80	$[I > 2\sigma(I)]$		
wR_2 (all data) 0.1197 0.1445 Goodness-of-fit (GOF) on F^2 1.02 0.80	$R_1 \left[I > 2\sigma(I) \right]$	0.0444	0.0423
Goodness-of-fit (GOF) on F^2 1.02 0.80	wR ₂ (all data)	0.1197	0.1445
	Goodness-of-fit (GOF) on F^2	1.02	0.80

2.6. General procedure for the Heck reaction

A mixture containing styrene (3.5 mmol), aryl halide (3.5 mmol), the palladium complex [(L)PdCl] (0.001 mmol) and potassium carbonate (8.0 mmol) in methanol (10 ml) were heated to reflux for 4 h. After evaporation of solvent the product was poured into water and extracted with diethyl ether. The ether solution was dried over Na_2SO_4 and filtered. The ether solution were passed through silica column (60–120 mesh), the complex remain trapped. After extraction of desired compound complex was extracted using dichloromethane. Upon evaporation of the ether, solid of pure products were obtained. The yields of the products obtained from all the reactions were determined after isolation and characterized by ¹H NMR spectra.

2.7. Crystallography

Single crystals of $[(L)_2Co]NO_3$ and $[(L)_2Ni]$ were grown by slow evaporation of methanol solution at 298 K. Data were collected by ω -scan technique on a Bruker Smart CCD diffractometer with Mo K α radiation monochromated by graphite crystal. Structure



Fig. 1. UV–Vis spectra of $[(L)_2Co]NO_3\ (^{\dots}),\ [(L)_2Ni]\ (-)$ and $[(L)PdCl]\ (-)$ in dichloromethane.

solution was done by direct method with SHELXS-97 program [51,52]. Full matrix least square refinements on F^2 were performed using SHELXL-97 program [51,52]. The fact to mention here that the crystal structure of compound [(L)₂Co]NO₃, **1** contain a disorder NO₃⁻ ion with refined occupancies for the O atoms of 0.555(11) & 0.445(11) and the crystal structure of compound [(L)₂Ni], **2** crystallizes with two independent complex molecules with two water molecules of crystallization per asymmetric unit. All non-hydrogen atoms were refined anisotropically using reflections $I > 2\sigma(I)$. The C-bound hydrogen atoms were included in calculated positions and refined as riding atoms. It was not possible to locate the water H atoms for compound **2**. Further crystallographic and refinement details are given in Table 1.

3. Results and discussion

3.1. Syntheses

The reactions of two equivalent of 2-((2-(benzylthio)phenylimino)methyl)phenol, HL ligand with Co(NO₃)₃.6H₂O and Ni(OAc)₂-·4H₂O separately in methanol afforded brown and green complexes of compositions [(L)₂Co]NO₃, **1**, and [(L)₂Ni], **2**, respectively (Scheme 1). The complex [(L)PdCl], **3** was synthesized upon reaction of ligand HL with Pd(MeCN)₂Cl₂ in 1:1 mol ratio in



Scheme 1. Synthesis of $[(L)_2M]^{n+}$ and [(L)PdCl].



Fig. 2. Molecular structure of $[(L)_2Co]^*$ with atom numbering scheme. Hydrogen atoms and NO₃⁻ ion are omitted for clarity.

acetonitrile solution. In all the complexes the ligand binds the metals in tridentate (O, N, S) fashion through deprotonated phenolic-O, imine-N and thioether-S atom forming two fused rings – one six membered and other five membered. The oxidation state of Co(III) in [(L)₂Co]NO₃, **1**, is satisfied by one NO₃⁻ ion. The composition of the complexes is supported by the microanalytical data and ¹H NMR spectra.

3.2. Spectral characterization and solution structures

Compounds **1–3** are soluble in common organic solvents furnishing brown, green and brown color respectively. UV–Vis spectra of the complexes were recorded in dichloromethane solutions and characteristic spectra for **1–3** are shown in Fig. 1. The UV–Vis spectral data are given in the experimental section. Compounds **1–3** displayed several absorptions in the visible and ultraviolet regions. Characteristic low energy absorption bands appeared near 445, 460 and 455 nm for $[(L)_2CO]NO_3$, $[(L)_2Ni]$ and [(L)PdCI] respectively which may be due to metal to ligand charge transfer (MLCT) (*vide DFT computation*).

The v(C=N) band in the ligand (1610 cm⁻¹) is shifted to lower frequency in all the complexes (1604–1606 cm⁻¹), indicating the coordination of the azomethine nitrogen [1]. Phenolic C–O band in ligand (1282 cm⁻¹) has been shifted to higher frequency in the complexes (1385–1389 cm⁻¹) indicating the coordination through the phenolic oxygen [1]. The v(C-S) near 758–752 cm⁻¹ indicates the coordination of the thio-benzyl group [1]. A broad band at 1337 cm⁻¹ was observed in cobalt(III) complex which is the

characteristic of uncoordinated NO_3^- [53]. The IR data are collected in Section 3.

The compositions of complexes [(L)₂Co]NO₃ and [(L)PdCl] matched well with the C, H, N analytical data and ¹H NMR spectral data. The O–H proton resonance is absent in the ¹HNMR spectra of [(L)₂Co]NO₃ and [(L)PdCl] complexes signifying the dissociation of the phenolic proton upon complexation. The singlet resonance for the aldimine (N=CH) proton of the HL ligand near δ = 8. 47 is shifted to δ = 7.94 and 8.23 in the cobalt(III) and Pd(II) complexes respectively [1]. The methylene proton resonance appeared as multiplet in the range δ 3.72–3.65 for complex [(L)₂Co]NO₃ whereas the methylene proton resonance of [(L)PdCl] appeared as two separate doublet at δ 4.49 and δ 4.33 due to the non equivalent nature of two methylene protons. The aromatic proton resonances of $[(L)_2Co]NO_3$ complex appeared as doublet at δ 7.56, multiplet in the range δ 7.32–7.20, triplet at δ 7.16, multiplet in the range δ 7.06–6.96, doublet at δ 6.76 and triplet at δ 6.56. The aromatic proton resonances of [(L)PdCl] appeared in the region δ 7.66–7.21 and one broad singlet at δ 6.64 for one proton. Although, all the aromatic protons for [(L)PdCl] could not be assigned accurately but the protons integrations matched well with the number of protons. The ¹H NMR data are given in Section 3.

3.3. X-ray structure determination of $[(L)_2Co]NO_3$ and $[(L)_2Ni]$

Suitable crystals of $[(L)_2Co]NO_3$ and $[(L)_2Ni]$ were grown by the slow evaporation of methanolic solutions. The X-ray structures of $[(L)_2Co]NO_3$, $[(L)_2Ni]$ were determined and the perspective view



Fig. 3. Molecular structure of [(L)₂Ni] with atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2		
Selected bond distances	(Å) and angles (deg)	for compound 1.

T-11- 0

Distances			
Co1-S1	2.2631(7)	N1-C7	1.290(3)
Co1-S2	2.2494(8)	N1-C8	1.432(3)
Co1-O1	1.8871(15)	N2-C28	1.433(3)
Co1-O2	1.8810(18)	N2-C27	1.295(3)
Co1-N1	1.9249(18)	O3-N3	1.262(7)
Co1-N2	1.9223(18)	02-C21	1.307(3)
S1-C13	1.769(2)	04-N3	1.209(8)
S1-C14	1.826(3)	05-N3	1.114(15)
01-C1	1.323(3)		
Angles			
S1-Co1-S2	85.89(3)	01-Co1-O2	88.93(7)
S1-Co1-O1	178.67(6)	01-Co1-N1	93.55(7)
S1-Co1-O2	92.38(5)	01-Co1-N2	86.84(7)
S1-Co1-N1	86.75(6)	02-Co1-N1	86.68(8)
S1-Co1-N2	92.83(6)	02-Co1-N2	94.51(8)
S2-Co1-O1	92.80(6)	N1-Co1-N2	178.75(10)
S2-Co1-O2	177.36(5)	Co1-S1-C13	97.40(8)
S2-Co1-N1	91.22(7)	Co1-S1-C14	110.55(10)
S2-Co1-N2	87.57(7)	C13-S1-C14	102.46(13)

of $[(L)_2Co]^+$ cation and the $[(L)_2Ni]$ molecule along with the atom numbering scheme are shown in Figs. 2 and 3 and selected bond distances and angles are collected in Tables 2 and 3. The asymmetric unit of $[(L)_2Ni]$ contains two molecules of same structural parameters. So, structural analysis of one molecule is considered. The geometry about the metal (Co(III) and Ni(II)) is distorted octahedral, where the two anionic ligands, $[L^-]$, coordinated meridionally giving rise to $MN_2O_2S_2$ (M = Co, Ni) coordination sphere. The three donor atoms are deprotonated phenolic oxygen, imine nitrogen and thioether sulfur. A disorder nitrate (NO_3^-) ion satisfies the unipositive charge of the complex cation, $[(L)_2Co]^+$. The orientations of phenolic-O, imine-N and thioether-S around metal

Table 3
Selected bond distances (Å) and angles (°) for compound 2 .

Distances			
Ni1-S1	2.4767(7)	Ni1-S2	2.5046(7)
Ni1-01	2.0103(16)	Ni1-02	1.9779(18)
Ni1-N1	2.0243(19)	Ni1-N2	2.0304(19)
S1-C13	1.778(3)	S1-C14	1.832(3)
S2-C34	1.832(3)	S2-C33	1.775(2)
01-C1	1.304(3)	02-C21	1.295(3)
N1-C7	1.297(3)	N1-C8	1.414(3)
N2-C28	1.420(3)	N2-C27	1.298(3)
Angles			
S1-Ni1-S2	92.50(2)	S1-Ni1-01	171.78(5)
S1-Ni1-O2	90.70(6)	S1-Ni1-N1	82.22(6)
Ni1-S1-C13	93.60(9)	S1-Ni1-N2	94.06(6)
S2-Ni1-01	83.58(5)	S2-Ni1-02	173.68(5)
Ni1-S2-C34	119.66(11)	S2-Ni1-N2	81.91(6)
S2-Ni1-N1	95.37(6)	01-Ni1-N1	90.93(7)
01-Ni1-02	93.90(7)	02-Ni1-N1	90.46(8)
01-Ni1-N2	92.54(7)	02-Ni1-N2	92.43(7)
N1-Ni1-N2	175.32(8)		

center are *cis,cis*; *trans,trans* and *cis,cis*, respectively. The Co(1)–O(1), Co(1)–N(1), Co(1)–S(1), and C(7)–N(1) lengths for $[(L)_2Co]^+$ (1.8870(15), 1.9249(18), 2.2631(7) and 1.290(3) Å, respectively) and Ni(1)–O(1), Ni(1)–N(1), Ni(1)–S(1), and C(7)–N(1) lengths for $[(L)_2Ni]$ (2.0103(16), 2.0243(19), 2.4767(7) and 1.297(3) Å, respectively) are within the normal range [40,54–56].

3.4. Electrochemistry

The electrochemical behavior of complex $[(L)_2Co]NO_3$ and $[(L)_2Ni]$ were investigated in dichloromethane acetonitrile mixed solvent (0.1 M TBAP) by cyclic voltammetry with a scan rate of 50 mV s⁻¹ (Figs. S6–S7). Complexes $[(L)_2Co]NO_3$ and $[(L)_2Ni]$ exhibited one electron quasireversible oxidative responses with the $E_{1/2}$



Fig. 4. Cyclic voltammogram of (a) [(L)₂Co]NO₃ and (b) [(L)₂Ni].





Fig. 5. (a) HOMO of $[(L)_2Co]^+$ and (b) LUMO of $[(L)_2Co]^+$; (c) HOMO of $[(L)_2Ni]$ and (d) LUMO of $[(L)_2Ni]$.

at 0.97 and 0.85 V versus SCE. The oxidation have been assigned according to the couple of Eqs. (1) and (2) where $[Co(L)_2]^+$ is the Co(III) analogue of $[Co(L)_2]^{2+}$ and $[Ni(L)_2]$ is analogue of $[Ni(L)_2]^+$ (see Fig. 4).

$$\left[(\mathbf{L})_2 \mathbf{Co} \right]^+ \rightleftharpoons \left[(\mathbf{L})_2 \mathbf{Co} \right]^{2+} \tag{1}$$

$$[(L)_2 Ni] \rightleftharpoons [(L)_2 Ni]^+$$
(2)

Table 4

Antibacterial activity of the cobalt compound [(L)2Co]NO3.

Strains	Sensitivity to the cobalt compound	Sensitivity to DMSO (control)	MIC (µg/ml)	MBC (µg/ml)
Escherichia coli DH5alpha	_	—	0.0	0.0
Bacillus subtilis ATCC6623	-	-	0.0	0.0
Staphylococcus ATCC25923	+	_	32	64

- Shows no antibacterial activity up to 200 µg/ml, - indicates no inhibition with DMSO.

Table 5Heck reaction with catalyst **3**.



Solvent = MeOH, base = K_2CO_3 , time = 4 h.

compound showed no antibacterial strains *Escherichia coli* DH5 and *Bacillus subtilis* ATCC6623 up to 200 µg/ml.

3.6. Heck reaction

Heck coupling is an important palladium catalyzed C–C coupling reaction where the substrates are arylhalides (bromoaryls and iodoaryls) and styrene [11,12]. We have examined the catalytic activity of [(L)PdCl] toward Heck coupling reactions in ambient condition. Conversions of arylhalides (Br and I) to corresponding stilbene derivatives upon reaction with styrene using [(L)PdCl] as catalyst in refluxing methanol and in presence of K₂CO₃ have been examined. The results of transformations are given in Table 5. After reaction the palladium catalyst was isolated and it was found that the coupling reactions did take place reusing the isolated catalyst. This reusability of the catalyst was checked up to three times for a reaction keeping the other conditions in tact. The products were characterized by ¹H NMR spectroscopy.

4. Conclusion

Ligand, 2-((2-(benzylthio)phenylimino)methyl)phenol, HL, is used for the synthesis of $[(L)_2Co]NO_3$, $[(L)_2Ni]$ and [(L)PdCl]. Complexes were characterized by usual spectroscopy and authenticated by X-ray structure determination on $[(L)_2Co]NO_3$, $[(L)_2Ni]$. The redox property of complexes $[(L)_2Co]NO_3$ and $[(L)_2Ni]$ were examined and correlate with DFT results. The new [(L)PdCl] complex have been used as catalysts for Heck coupling reactions in presence of air and moisture. The compound $[Co(L)_2]NO_3$ is tested for *in vitro* antibacterial activity.

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 $X = I \text{ or } Br \quad R = H, Me, NO_2$

According to the DFT results the composition of HOMO (Fig. 5(a and c)) of $[(L)_2Co]NO_3$ and $[(L)_2Ni]$ are metal centered indicating the oxidation to be metal centered. The LUMO (Fig. 5(b and d)) are metal ligand mixed centered. Therefore the HOMO \rightarrow LUMO MLCT transition is consistent with the assignment of UV–Vis spectra.

3.5. Antibacterial activity

The compound of cobalt $[(L)_2Co]NO_3$ was found to show good *in vitro* activity to one bacterial strain-*Staphylococcus* ATCC25923, out of the three bacterial strains used in this work (Table 4). Data revealed that the compound inhibited *Staphylococcus aureus* MIC 32 µg/ml and MBC was found to be 64 µg/ml. However the

authors are grateful to Prof. P.K. Bag, Department of Biochemistry, University of Calcutta, for his valuable guidance during the study of microbial activity. Author PP acknowledged to DST under WOS-A (Sanction No. SR/WOS-140/2011) and JP acknowledged to University Grants Commission (under Minor Research Project, Sanction No. F.PSW/067/2011-12). The necessary laboratory and infrastructural facility are provided by the Department of Chemistry, Kandi Raj College and Department of Chemistry, University of Kalyani.

Appendix A. Supplementary material

CCDC 806268 and 912712; contain the supplementary crystallographic data for **1–3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the

(3)

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2013.01.010.

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