



Synthesis and characterization of copper(II) and cobalt(II) complexes with two new potentially hexadentate Schiff base ligands. X-ray crystal structure determination of one copper(II) complex

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ABSTRACT

Two new potentially hexadentate N₂O₄ Schiff base ligands 2-((z)-(2-(2-((z)-3,5-di-*tert*-butyl-2-hydroxybenzylideneamino) phenoxy) phenylimino) methyl)-4,6-di-*tert*-butylphenol [H₂L¹] and 2-((z)-(2-(2-((z)-3,5-di-*tert*-butyl-2-hydroxybenzylideneamino) phenoxy)-5-*tert*-butylphenoxy) phenylimino) methyl)-4,6-di-*tert*-butylphenol [H₂L²] were prepared from the reaction of 3,5-di-*tert*-butyl-2-hydroxy benzaldehyde with 1,2-bis(2'-aminophenoxy)benzene or 1,2-bis(2'-aminophenoxy)-4-*t*-butylbenzene, respectively. From the direct reaction of ligands [H₂L¹] and [H₂L²] with copper(II) and cobalt(II) salts in methanolic solution and in the presence of N(Et)₃ the neutral [CuL¹], [CuL²], [CoL¹] and [CoL²] complexes were prepared. All complexes were characterized by IR spectra, elemental analysis, magnetic susceptibility, mass spectra, molar conductance (Λ_m), UV-Vis spectra and in the case of [CuL²] with X-ray diffraction. X-ray crystal structure of [CuL²] showed that the complex contains copper(II) in a distorted square planar environment of N₂O₂ donors. Three CH/ π interactions were observed in the molecular structure of latter complex.

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1. Introduction

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. In the area of bioinorganic chemistry interest in Schiff base complexes has centered on the role of such complexes in providing synthetic models for the metal containing sites in metallo-proteins and enzymes [1–5]. Schiff base ligands are potential anticancer drugs [6] and the anticancer activity of this metal complexes is enhanced in comparison to the free ligand [7]. 2-Hydroxy Schiff base ligands and their complexes derived from the reaction of derivatives of salicylaldehyde with amines have been extensively studied in great details for their various crystallographic, structural and magnetic features [8–10]. The cobalt(II) and manganese(II) complexes with tetra dentate Schiff base ligands which coordinate through N₂O₂ donor atoms have been extensively studied as oxygen carriers and also as catalyst for water splitting system [11,12]. In the present paper, the synthesis of diamines [1,2-bis(2'-aminophenoxy)benzene(III) and 1,2-bis(2'-aminophenoxy)-4-*t*-butylbenzene(IV)], potentially

hexadentate Schiff base ligands [H₂L¹] and [H₂L²] (Scheme 1) and their Cu(II) and Co(II) complexes are described. X-ray crystal structure [CuL²] complex showed that the oxygen donor atoms and nitrogen donor atoms are *trans* to each other.

2. Experimental

2.1. Starting materials

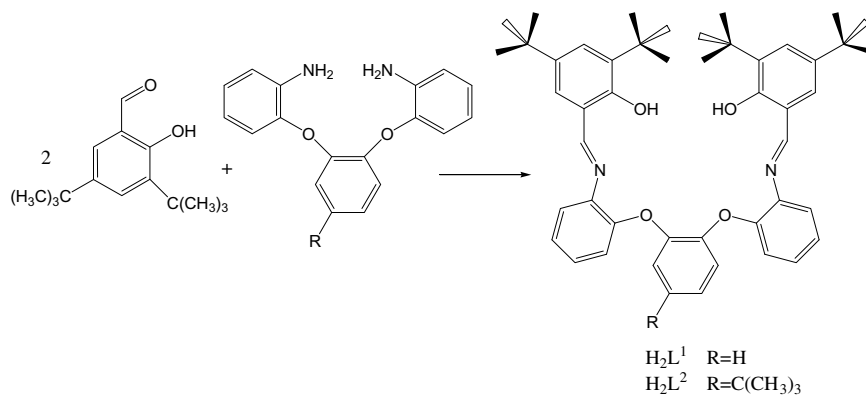
3,5-Di-*tert*-butyl-2-hydroxy benzaldehyde was synthesized according to the literature procedure [13]. Solvents, Catechol, 4-*tert*-butylcatechol, 1-fluoro-2-nitrobenzene and metal salts were purchased from Merck and were used without further purification.

2.2. Physical measurements

Infrared spectra were collected using KBr pellets on a BIO-RAD FTS-40A spectrophotometer (400–4000 cm⁻¹). A Perkin-Elmer, Lambda 45 (UV-Vis) spectrophotometer was used to record the electronic spectra. Electron impact (20 eV) mass spectra for ligands were recorded on a Shimadzu, QP1100EX spectrometer. FAB mass spectra were recorded using a Kratos-MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the

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Scheme 1.

matrix. The Magnetic susceptibility measurements were performed at 25 °C using a Johnson Matthey Alfa MSB MKI Gouy balance. CHN analyses were carried out using a Perkin–Elmer, CHNS/O elemental analyzer model 2400. Conductance measurements were performed using a Hanna HI 8820 conductivity meter. ¹H and ¹³C NMR spectra were taken in CDCl₃ on a Bruker Avance 300 MHz and Jeol 90 MHz spectrometer using Si(CH₃)₄ as an internal standard.

2.3. X-ray crystallography

Single crystal of [CuL²] complex was obtained from toluene by acetonitrile diffusion method. The single crystal X-ray diffraction analyses were performed on a STOE IPDS-II two circle diffractometer at 293(2) K, using graphite monochromated Mo K α X-ray radiation ($\lambda = 0.7107$ nm). Details of the X-ray experiments and crystal data are summarized in Table 1.

2.4. Synthesis

2.4.1. Synthesis of 1,2-bis(2'-nitrophenoxy)benzene (I)

Catechol (11 g, 0.1 mol) was dissolved in DMF/Xylene mixture before K₂CO₃ (42 g, 0.3 mol) and 1-fluoro-2-nitrobenzene (28.2 g, 0.2 mol) were added. The mixture, refluxed at 130–135 °C under a dinitrogen atmosphere for 12 h with stirring, was then allowed to cool and poured into 500 ml of H₂O. The precipitate was isolated by filtration. After drying, the crude product was recrystallized from EtOH to give pure 1,2-bis(2'-nitrophenoxy)benzene. Yield: 31.3 g (89%). M.p. 110 °C. Anal. Calc. for C₁₈H₁₂N₂O₆: C, 61.4; H, 3.4; N, 7.9. Found: C, 61.3; H, 3.5; N, 7.8%. IR(cm⁻¹, KBr): 1524, 1348 (s, ν NO₂).

2.4.2. Synthesis of 1,2-bis(2'-nitrophenoxy)-4-*t*-butylbenzene (II)

4-*tert*-Butylcatechol (16.6 g, 0.1 mol) was dissolved in DMF/Xylene mixture before K₂CO₃ (42 g, 0.3 mol) and 1-fluoro-2-nitrobenzene (28.2 g, 0.2 mol) were added. The mixture was refluxed at 130–135 °C under a dinitrogen atmosphere for 12 h with stirring. The obtained mixture was poured into 500 ml of MeOH/H₂O (vol ratio 10:1) and left overnight in 0 °C to give a solid, which was collected, washed thoroughly with MeOH and H₂O and dried under vacuum. After drying, the crude product was recrystallized with EtOH to give pure 1,2-bis(2'-nitrophenoxy)-4-*t*-butylbenzene. Yield: 37.2 g (91%). M.p. 52 °C. Anal. Calc. for C₂₂H₂₀N₂O₆: C, 64.7; H, 4.9; N, 6.9. Found: C, 64.7; H, 4.9; N, 6.9%. IR(cm⁻¹, KBr): 2964, 2868 (C–H)aliph, 1524, 1348 (s, ν NO₂).

2.4.3. Synthesis of 1,2-bis(2'-aminophenoxy)benzene (III)

A mixture of 1,2-bis(2'-nitrophenoxy) benzene (3.52 g, 10 mmol), NH₄Cl (1.07 g, 20 mmol) and 10 ml of H₂O in 100 ml

of EtOH was heated to boiling and zinc dust (2 g, 30 mmol) in 0.1 g portions at intervals of several minutes was added. The mixture was then refluxed for 5 h. The resulting solution was filtered, extracted with 300 ml H₂O and dried. The precipitate was dissolved in CH₃CN, The solution was filtered and the solvent was then removed. Yield: 2.1 g (73%). M.p. 110 °C. Anal. Calc. for C₁₈H₁₆N₂O₂·0.25H₂O: C, 72.8; H, 5.6; N, 9.4. Found: C, 72.7; H, 5.5; N, 9.5%. IR(cm⁻¹, KBr): 3426, 3408, 3313 (NH str).

2.4.4. Synthesis of 1,2-bis(2'-aminophenoxy)-4-*t*-butylbenzene (IV)

A mixture of 1,2-bis(2'-nitrophenoxy)-4-*t*-butylbenzene (4.09 g, 10 mmol), NH₄Cl (1.07 g, 20 mmol) and 10 ml of H₂O in 100 ml of EtOH was heated to boiling and zinc dust (2 g, 30 mmol) in 0.1 g portions at intervals of several minutes. The mixture was refluxed for 5 h. The solution was evaporated to dryness and the residue extracted with H₂O/CHCl₃. The organic layer was evaporated to yield an organic solid. Yield: 2.7 g (77%). M.p. 89–91 °C. Anal. Calc. for C₂₂H₂₄N₂O₂·H₂O: C, 72.1; H, 7.1; N, 7.6. Found: C, 72.2; H, 7.1; N, 7.7%. IR(cm⁻¹, KBr): 3461, 3405, 3376, 3304 (–NH₂), 3041 (C–H)ar, 2962, 2867 (C–H)aliph.

2.4.5. H₂L¹

1,2-bis(2'-aminophenoxy) benzene (0.292 g, 1 mmol) in methanol (20 ml) was added dropwise with stirring to a solution of 3,5-di-*tert*-butyl-2-hydroxy benzaldehyde (0.468 g, 2 mmol) in methanol (30 ml). The mixture was stirred and heated to reflux for 4 h. A yellow precipitate was obtained that was filtered off and washed with cold methanol and dried in vacuo. Yield: 0.5 g (69%). M.p. 176 °C. Anal. Calc. for C₄₈H₅₆N₂O₄: C, 79.5; H, 7.8; N, 3.9. Found: C, 79.1; H, 7.2; N, 4.3%. IR (cm⁻¹, KBr): 1620 (s, ν C=N). UV–Vis [λ (nm), ϵ (M⁻¹ cm⁻¹)]: 279(45 390), 338(33 600), 365(sh). Mass spectral parent ion; m/z 724.

2.4.6. H₂L²

In a manner similar to the above-mentioned a methanol solution (20 ml) of 1,2-bis(2'-aminophenoxy)-4-*t*-butylbenzene (0.348 g, 1 mmol) was added dropwise with stirring to a solution of 3,5-di-*tert*-butyl-2-hydroxy benzaldehyde (0.468 g, 2 mmol) in methanol (30 ml). The mixture was stirred and heated to reflux for 4 h. A yellow solid product was formed that washed with cold methanol and dried in vacuo. Yield: 0.6 g (77%). M.p. 105 °C. Anal. Calc. for C₅₂H₆₄N₂O₄: C, 79.9; H, 8.3; N, 3.6. Found: C, 79.3; H, 8.2; N, 2.9%. IR (cm⁻¹, KBr): 1620 (s, ν C=N). UV–Vis [λ (nm), ϵ (M⁻¹ cm⁻¹)]: 278(29 040), 345(21 390), 362(sh). Mass spectral parent ion; m/z 781.

2.4.7. [CuL¹]

A methanol solution (15 ml) of Cu(ClO₄)₂·6H₂O (0.3704 g, 1 mmol) and a moderate excess of N(Et)₃ were added to a warm

solution of $[H_2L^1]$ (0.724 g, 1 mmol) in methanol (50 ml). The mixture was stirred and heated to reflux for 4 h. The resultant green solid product was collected by filtration and washed with cold methanol. Green crystals of $[CuL^1]$ were obtained by liquid diffusion of acetonitrile into a solution of the complex in toluene. Yield: 0.5 g (64%). M.p. 328 °C. Anal. Calc. for $C_{48}H_{54}CuN_2O_4$: C, 73.3; H, 6.9; N, 3.6. Found: C, 72.8; H, 6.9; N, 4.2%. IR (cm^{-1} , KBr): 1613 (s, $\nu_{C=N}$), 443–470 (M–O), 535 (M–N). UV–Vis [λ (nm), ϵ ($M^{-1} cm^{-1}$)]: 244(41090), 306(30330), 427(11620), 692(104). $\Lambda_m = 5 cm^2 \Omega^{-1} mol^{-1}$. FAB-MS (m/z): 785($[CuL^1 + H]^+$, 100%).

2.4.8. $[CuL^2]$

Similarly, $[H_2L^2]$ (0.780, 1 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ yielded the product as green crystals. Yield: 0.7 g (83%). M.p. 316 °C. Anal. Calc. for $C_{52}H_{62}CuN_2O_4$: C, 74.1; H, 7.4; N, 3.3. Found: C, 74.6; H, 7.1; N, 3.8%. IR (cm^{-1} , KBr): 1613 (s, $\nu_{C=N}$), 445–470 (M–O), 535 (M–N). UV–Vis [λ (nm), ϵ ($M^{-1} cm^{-1}$)]: 245(44740), 296(31740), 425(13490), 688(110). $\Lambda_m = 4.2 cm^2 \Omega^{-1} mol^{-1}$. FAB-MS (m/z): 841($[CuL^2 + H]^+$, 100%).

2.4.9. $[CoL^1]$

In the same way, a methanol solution (15 ml) of $CoCl_2 \cdot 6H_2O$ (0.2378 g, 1 mmol) and a moderate excess of $N(Et)_3$ were added

to a warm solution of $[H_2L^1]$ (0.724 g, 1 mmol) in methanol (50 ml). The resultant red solid was collected by filtration and washed with cold methanol. Red crystals of $[CoL^1]$ were obtained by liquid diffusion of methanol into a solution of the complex in toluene. Yield: 0.6 g (77%). M.p. 309 °C. Anal. Calc. for $C_{48}H_{54}CoN_2O_4$: C, 73.7; H, 6.9; N, 3.6. Found: C, 72.9; H, 6.9; N, 2.9%. IR (cm^{-1} , KBr): 1615 (s, $\nu_{C=N}$), 445–472 (M–O), 537 (M–N). UV–Vis [λ (nm), ϵ ($M^{-1} cm^{-1}$)]: 289(28430), 336(19310), 429(14600), 578(179), 885(29). $\Lambda_m = 2.5 cm^2 \Omega^{-1} mol^{-1}$. FAB-MS (m/z): 782($[CoL^1]$, 100%).

2.4.10. $[CoL^2]$

Similarly, $[H_2L^2]$ (0.780, 1 mmol) and $CoCl_2 \cdot 6H_2O$ (0.2378 g, 1 mmol) yielded the product as red crystals. Yield: 0.7 g (84%). M.p. 290 °C. Anal. Calc. for $C_{52}H_{62}CoN_2O_4$: C, 74.5; H, 7.5; N, 3.3. Found: C, 74.8; H, 7.8; N, 2.9%. IR (cm^{-1} , KBr): 1614 (s, $\nu_{C=N}$), 443–477 (M–O), 538 (M–N). UV–Vis [λ (nm), ϵ ($M^{-1} cm^{-1}$)]: 288(30600), 335(21900), 436(15760), 567(186), 897(26). $\Lambda_m = 1.8 cm^2 \Omega^{-1} mol^{-1}$. FAB-MS (m/z): 837($[CoL^2 + H]^+$, 100%).

3. Results and discussion

Two new potentially hexadentate N_2O_4 Schiff base ligands $[H_2L^1]$ and $[H_2L^2]$ have been easily prepared from the reaction of 3,5-di-*tert*-butyl-2-hydroxy benzaldehyde with 1,2-bis(2'-amino-phenoxy) benzene or 1,2-bis(2'-aminophenoxy)-4-*t*-butylbenzene, respectively. The analytical and spectral data are completely consistent with the proposed formulation. The 1H NMR and $^{13}C\{^1H\}$ NMR assignments for 1,2-bis(2'-nitrophenoxy)benzene (I), 1,2-bis(2'-nitrophenoxy)-4-*t*-butylbenzene (II), 1,2-bis(2'-aminophenoxy)benzene (III), 1,2-bis(2'-aminophenoxy)-4-*t*-butylbenzene (IV), $[H_2L^1]$ and $[H_2L^2]$ are given in Table 4. The neutral Cu(II) and Co(II) complexes of these ligands, were also synthesized. All complexes were characterized by IR spectra, elemental analysis, magnetic susceptibility measurements, mass spectra, molar conductance (Λ_m), UV–Vis spectra and in the case of $[CuL^2]$ with X-ray diffraction. The corresponding data for the ligands and their complexes are presented in Tables 2–6.

3.1. IR spectra

1,2-Bis(2'-nitrophenoxy)benzene (I) and 1,2-bis(2'-nitrophenoxy)-4-*t*-butylbenzene (II) can be prepared by S_NAr between 1-fluoro-2-nitrobenzene and simple aromatic diols (catechol or 4-*tert*-butylcatechol). The IR spectrum of (I) and (II) reveals absorption bands appearing at ca. 1348 and 1524 cm^{-1} due to symmetric and asymmetric stretching of $-NO_2$ group [14–16]. Aromatic nitro compounds can be reduced in high yield to the corresponding diamines using zinc metal and NH_4Cl in $H_2O/EtOH$ [17–26]. After reduction, the characteristic absorptions of nitro groups disappeared and the amino groups showed NH stretching bands at 3313, 3408, 3426 cm^{-1} and 3304, 3376, 3405, 3461 cm^{-1} for (III) and (IV), respectively. The infrared spectra of $[H_2L^1]$ and $[H_2L^2]$ in the region 400–4000 cm^{-1} show a strong absorption band at

Table 1
Crystal data and structure refinement for the $[CuL^2]$

Empirical formula	$C_{52}H_{62}CuN_2O_4$
Formula weight	842.59
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
<i>a</i> (Å)	19.043(4)
<i>b</i> (Å)	14.744(3)
<i>c</i> (Å)	18.667(4)
α (°)	90
β (°)	119.35(3)
γ (°)	90
Volume (Å ³)	4568 (2)
<i>Z</i>	4
Calculated density (Mg/m ³)	1.225
Absorption coefficient (mm ^{−1})	0.524
<i>F</i> (000)	1796
Crystal size (mm)	0.4 × 0.22 × 0.08
θ Range for data collection (°)	1.85–30.58
Limiting indices	−27 ≤ <i>h</i> ≤ 27, −21 ≤ <i>k</i> ≤ 21, −26 ≤ <i>l</i> ≤ 26
Reflections collected/unique [<i>R</i> _{int}]	54823/12352 [0.1142]
Completeness to $\Theta = 30.58$ (%)	98.0
Absorption correction	Numerical
Maximum and minimum transmission	0.97 and 0.87
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	12352/0/533
Goodness-of-fit on <i>F</i> ²	1.078
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0804, <i>wR</i> ₂ = 0.1847
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1074, <i>wR</i> ₂ = 0.2014
Largest difference peak and hole (e Å ^{−3})	0.797 and −1.262

Table 2
Physical characterization, analytical, molar conductance, mass spectra and magnetic susceptibility data of the complexes

Compound	Found (calc.)			Yield (%)	Color	Mol weight	Λ_m ($\Omega^{-1} cm^2 mol^{-1}$)	Fab-MS	Assignment	μ_{eff} (BM)
	%C	%H	%N							
$C_{48}H_{56}N_2O_4$	(79.5)79.1	(7.8)7.2	(3.9)4.3	69	Yellow	724.97		724	$[H_2L^1+H]^+$	
$C_{52}H_{64}N_2O_4$	(79.9)79.3	(8.3) 8.2	(3.6)2.9	77	Yellow	781.08		781	$[H_2L^2]$	
CuL^1	(73.3)72.8	(6.9)6.9	(3.6)4.2	64	Green	786.49	5	785	$[CuL^1+H]^+$	1.54
CoL^1	(73.7)72.9	(6.9)6.9	(3.6)2.9	77	Red	781.89	2.5	782	$[CoL^1]$	4.48
CuL^2	(74.1)74.6	(7.4)7.1	(3.3)3.8	83	Green	842.59	4.2	841	$[CuL^2+H]^+$	2.02
CoL^2	(74.5)74.8	(7.5)7.8	(3.3)2.9	84	Red	837.99	1.8	837	$[CoL^2+H]^+$	4.38

Table 3
Comparison of IR data (cm⁻¹) for [H₂L¹] and [H₂L²] ligands and related complexes

[H ₂ L ¹]	[H ₂ L ²]	[CuL ¹]	[CoL ²]	[CoL ¹]	[CuL ²]
1620(s)	1620(s)	1613(s)	1614(s)	1615(s)	1613(s)
1581(s)	1581(s), 1503(m)	1588(s), 1545(m)	1582(s), 1542(m)	1580(s), 1545(m)	1588(s), 1544(m)
1489(s)	1489(s)	1527(s), 1490(s)	1526(s), 1487(s)	1526(s), 1489(s)	1527(s), 1486(s)
1470(m), 1453(m)	1467(m), 1453(m)	1454(s), 1426(s)	1459(s), 1424(s)	1455(s), 1423(s)	1458(s), 1427(s)
1441(m), 1390(m)	1440(m), 1393(m)	1407(w), 1384(s)	1400(m), 1384(s)	1410(w), 1386(s)	1413(w), 1385(s)
1361(s), 1315(w)	1363(s), 1319(w)	1359(s), 1324(m)	1361(s), 1331(m)	1360(s), 1331(m)	1360(s), 1326(m)
1263(s)	1272(s), 1250(m)	1274(w), 1256(s)	1268(w), 1255(s)	1274(w), 1256(s)	1271(w), 1255(s)
1230(m)	1230(m)	1230(s)	1241(w), 1227(s)	1242(w), 1227(s)	1244(w), 1230(s)
1209(w), 1192(m)	1203(w)	1203(s), 1185(w)	1201(s), 1183(w)	1201(s), 1182(w)	1203(s), 1183(w)
1169(s), 1131(w)	1168(s), 1128(w)	1164(s), 1134(m)	1162(s), 1133(m)	1162(s), 1133(m)	1164(s), 1133(m)
1109(m)	1109(m)	1109(m)	1109(m)	1109(m)	1109(m)
1042(w), 1026(w)	1041(w), 1027(w)	1037(w), 1027(w)	1046(w), 1027(w)	1048(w), 1028(w)	1037(w), 1025(w)
982(w), 927(w)	981(w), 943(w)	976(w), 933(w)	974(w), 941(w)	971(w), 932(w)	977(w), 943(w)
900(w), 882(w)	901(w), 880(w)	918(w), 875(m)	920(w), 887(w)	917(w), 885(w)	907(w), 885(w)
865(w)	844(m)	861(w)	876(m), 848(w)	870(m)	873(w), 850(w)
849(w), 821(w)	844(w), 822(w)	834(m), 811(w)	832(m), 810(w)	836(m), 810(w)	833(m), 817(w)
795(w), 774(w)	803(w), 774(w)	788(m), 761(w)	790(m)	790(m)	788(m)
745(s)	749(s)	749(w), 740(s)	753(w), 745(s)	747(s)	753(s)
693(w), 670(w)	694(w), 666(m)	694(w), 658(w)	695(w), 667(w)	693(w)	699(w)
645(w)	645(w)	637(w)	636(w)	634(w)	636(w)

Table 4
¹H NMR and ¹³C[¹H] NMR data for dinitro and diamine compounds, [H₂L¹] and [H₂L²] ligands

Hydrogen atoms	Carbon atoms		
(I)			
6.975–7.999	(m, 12H, aromatics)	(aromatic rings)	118.880, 121.641, 123.117 125.476, 126.279, 134.263 140.007, 145.816, 150.095
(II)			
6.846–7.848	(m, 11H, aromatics)	C ₁ ,	31.095
1.312	(s, 9H, H ₁)	C ₂ ,	34.557
		(aromatic rings)	117.995, 118.480, 119.807 121.666, 122.579, 122.794 123.448, 125.404, 134.117 139.511, 139.782, 143.250 144.682, 150.308
(III)			
6.616–7.042	(m, 12H, aromatics)	(aromatic rings)	116.820, 117.811, 118.858
3.663	(s, 4H, NH ₂)		120.088, 124.162, 137.492 144.336, 147.209
(IV)			
6.659–7.147	(m, 11H, aromatics)	C ₁ ,	31.689
3.658–3.664	(b, 4H, NH ₂)	C ₂ ,	35.119
1.279	(s, 9H, H ₁)	(aromatic rings)	116.937, 118.133, 118.529 119.224, 119.757, 122.107 124.948, 125.363, 139.697 140.073, 144.571, 145.169 146.374, 147.312, 148.507
H ₂ L ¹			
13.209	(s, 2H, OH)	C ₁ , C ₇	31.632, 29.576
8.336	(s, 2H, CH=N)	C ₂ , C ₆	35.184, 34.263
6.816–7.330	(m, 16H, aromatics)	C ₈	158.474
1.349	(s, 18H, H ₇)	C ₁₁	165.123
1.229	(s, 18H, H ₁)	(aromatic rings)	118.298, 118.602, 121.254 121.537, 123.700, 124.950 126.938, 127.183, 127.845 136.984, 139.299, 140.268 147.290, 149.927
H ₂ L ²			
13.342	(s, 2H, OH)	C ₁ , C ₇ , C ₂₂ , C ₃₇ , C ₄₁	29.592, 31.562, 31.617
8.409	(s, 1H, CH=N)	C ₂ , C ₆ , C ₂₁ , C ₃₆ , C ₄₀	34.236, 34.571, 35.160
8.428	(s, 1H, CH=N)	C ₈ , C ₄₂	158.436
6.865–7.430	(m, 15H, aromatics)	C ₁₁ , C ₃₂	165.123
1.470	(s, 9H, H ₂₂)	(aromatic rings)	117.531, 117.960, 118.618
1.351	(s, 18H, H ₇ , ₄₁)		119.171, 121.259, 121.995
1.314	(s, 18H, H _{1,37})		123.314, 123.442, 126.926 127.066, 127.732, 136.936 138.942, 139.123, 140.204 144.772, 146.023, 148.639 150.087

s, singlet; m, multiplet, b, broad.

Table 5
Electronic spectroscopy data (nm) for H_2L^{1-2} and related complexes

Compound	λ_{max} (nm) (ϵ) ^a		
	Intraligand (LL)	CT	d-d
[H_2L^1]	279 (45,390)	338 (33,600), 365(sh)	
[H_2L^2]	278 (29,040)	345 (21,390), 362(sh)	
[CuL^1]	244 (41,090)	306 (30,330)	692 (104) ^b
[CuL^2]	245 (44,740)	296 (31,740)	688 (110) ^b
[CoL^1]	289 (28,430)	336 (19,310)	578 (179) ^b
[CoL^2]	288 (30,600)	335 (21,900)	567 (186) ^b

^a $Mol^{-1} cm^{-1}$.^b Shoulder.**Table 6**
Selected bond lengths (Å) and bond angles (°) for [CuL^2]

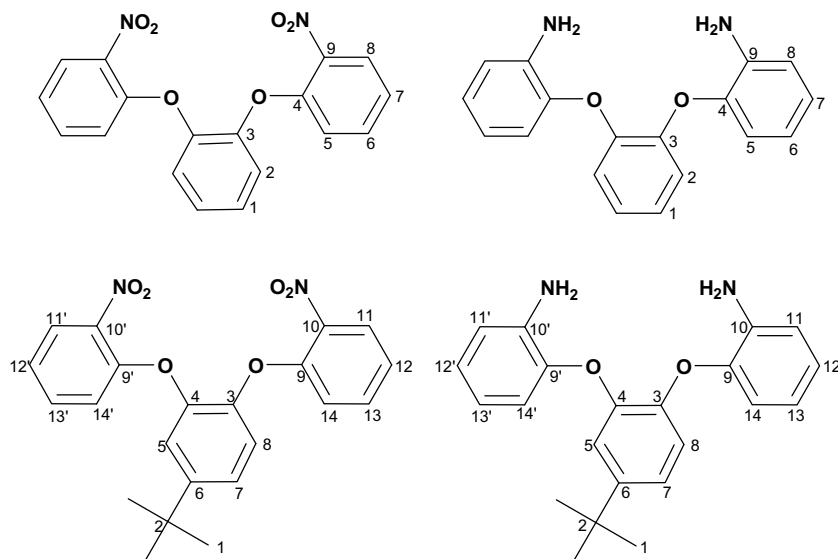
Bond lengths	
Cu(1)–O(1)	1.849(2)
Cu(1)–O(4)	1.884(2)
Cu(1)–N(1)	2.024(3)
Cu(1)–N(2)	2.038(3)
Cu(1)–O(2)	2.846(3)
Cu(1)–O(3)	3.161(2)
Bond angles	
O(1)–Cu(1)–O(4)	152.01(10)
O(1)–Cu(1)–N(1)	89.80(11)
O(4)–Cu(1)–N(1)	92.96(11)
O(1)–Cu(1)–N(2)	94.77(11)
O(4)–Cu(1)–N(2)	89.89(11)
N(1)–Cu(1)–N(2)	164.59(11)

1620 cm^{-1} assigned to the C=N stretching vibration, indicating the formation of the Schiff base linkages. Furthermore, the absence of C=O and N–H stretching vibrations in the spectra of the ligands, related to aldehyde and diamine, respectively, indicate occurrence of Schiff base condensation. The reaction of copper(II) or cobalt(II) salts with the Schiff base ligands ($[H_2L^1]$ and $[H_2L^2]$) yields [CuL^1], [CuL^2], [CoL^1] and [CoL^2] complexes. Deprotonation of all phenolic functions is confirmed by the lack of O–H stretching bands in the IR region 3300–3400 cm^{-1} for all the complexes [27,28]. The infrared spectra of these complexes provide some information about the bonding in the complexes. The strong $\nu(C=N)$ bands are shifted towards lower frequencies compared with free imine bonds, indicating coordination of the ligands to the copper(II) and cobalt(II) ions via the azomethine nitrogen atoms. The bands at 1169 cm^{-1} for

$[H_2L^1]$ and 1168 cm^{-1} for $[H_2L^2]$ are ascribed to the phenolic C–O stretching vibrations. These bands are shifted to lower frequencies due to O–metal coordination. The coordination of the azomethine nitrogen is confirmed with the presence of a new band between 532 and 559 cm^{-1} , assignable to $\nu(M-N)$ for the Co(II) and Cu(II) complexes [29,30]. Several medium to strong absorption bands appear in the far-IR spectra of mentioned complexes (between 443 and 477 cm^{-1}), due to $\nu(M-O)$ [31,32]. The full IR spectral data (600–1700 cm^{-1}) for ligands and related complexes are compared in Table 3. As can be seen, the IR spectra of the copper complexes are very similar to each other and this is the case for corresponding cobalt complexes, indicating the same structures [33].

3.2. Magnetic measurements

Room temperature magnetic moments of the Cu(II) complexes are 1.54 and 2.02 BM for [CuL^1] and [CuL^2], respectively. The observed value for [CuL^2] is typical for mononuclear compounds of Cu(II) with a $S = 1/2$ spin state and does not indicate antiferromagnetic coupling of the spins at this temperature [34]. The smaller value of the magnetic moment of [CuL^1] is probably due to a weak intermolecular antiferromagnetic exchange interaction between the copper centers in the crystal structure [35]. Note that such interactions between the copper centers mononuclear [CuL^1] complex is due to the lack of bulky *t*-butyl group in this compound, in contrast to [CuL^2]. Magnetic susceptibility studies reveal complexes [CoL^1] and [CoL^2] to be paramagnetic, with μ_{eff} values of 4.48 and 4.38 BM, respectively. The observed magnetic moments are consist with that expected for four coordinate Co(II) tetrahedral complexes [36–38].

**Fig. 1.** Structure of dinitro and diamine compounds along with NMR numbering.

3.3. NMR spectra

The ^1H and ^{13}C NMR spectra of the dinitro compounds, diamines and ligands in CDCl_3 solution confirm their proposed structures.

The NMR numbering of the atoms is shown in Fig. 1. for dinitro and diamines compounds and Fig. 2. for ligands. In the ^1H NMR spectrum, the absorption signals of aromatic protons of (I) and (II) appeared in the region of 6.975–7.999 ppm and 6.846–

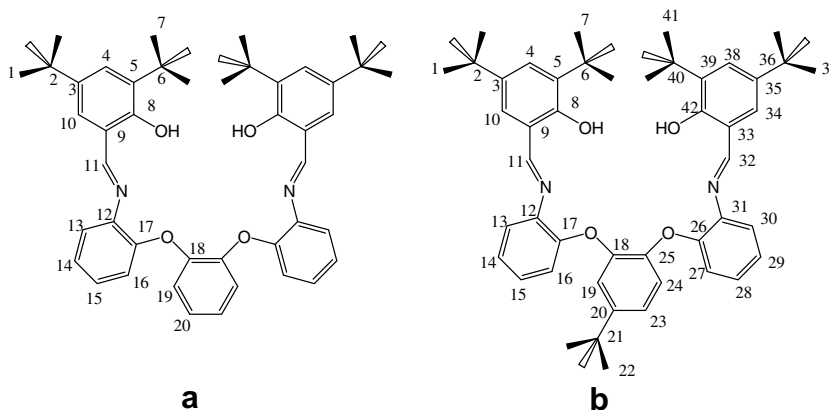


Fig. 2. Structure of (a) $[\text{H}_2\text{L}^1]$ and (b) $[\text{H}_2\text{L}^2]$, along with NMR numbering.

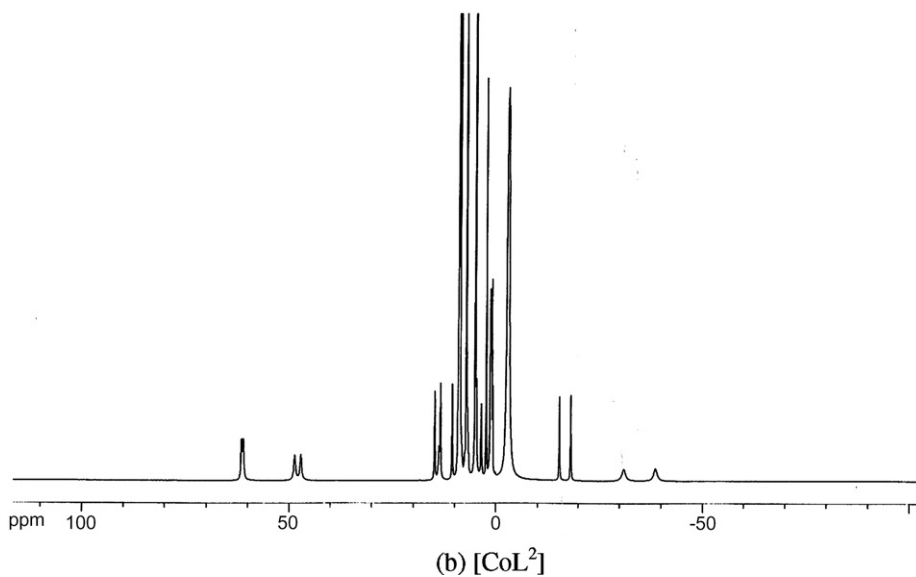
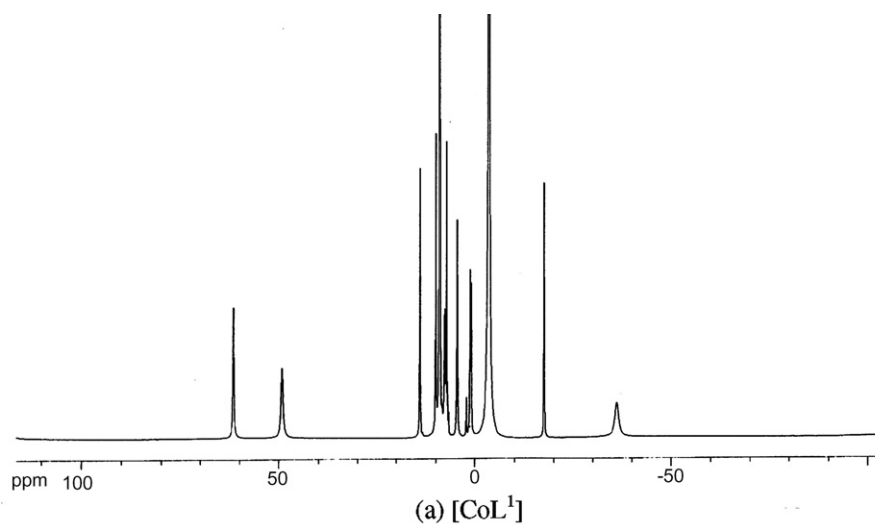


Fig. 3. ^1H NMR spectra of (a) $[\text{CoL}^1]$ and (b) $[\text{CoL}^2]$.

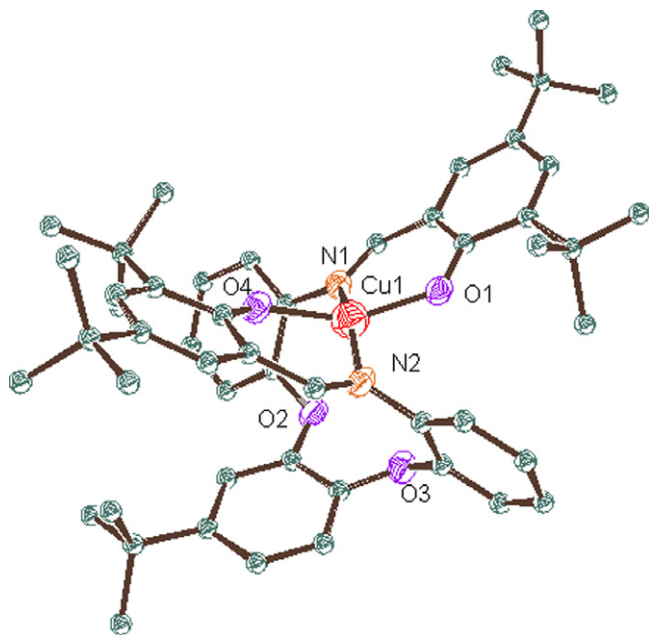


Fig. 4. Molecular structure of the $[\text{CuL}^2]$. Hydrogen atoms are omitted for clarity.

7.848 ppm, respectively, and the *t*-butyl group of (II) appeared in 1.312 ppm. In ^{13}C NMR spectrum should be exhibited 20 main peaks for (II). However, there are 16 main signals appeared, it seems the carbon C_9 , C_{10} , C_{11} and C_{13} are overlapping with C_9 , C_{10} , C_{11} and C_{13} , respectively, and the numbers of C were still conformed to (II). The ^{13}C NMR in (I) showed nine aromatic signals, the number of carbons was conformed to the (I). In the ^1H NMR spectra, all the aromatic protons of (III) and (IV) resonated in the 6.616–7.042 ppm and 6.659–7.147 ppm region, respectively. Hydrogens of the *t*-butyl group appeared in 1.279 ppm and the signal appearing at 3.658–3.664 ppm corresponding to the amine group. Comparing the ^{13}C NMR spectra of (III) and (IV) with the spectra of its precursor (I) and (II), the ^{13}C absorptions of the central three benzene rings move upfield as a result of the transfer of electron-withdrawing nitro groups to the electron-donating amino groups [14,15]. The ^1H NMR spectrum of the ligand $[\text{H}_2\text{L}^1]$ shows only a single ^1H imine resonance at ca. 8.336 ppm, demonstrating the equivalence of the two imine environments. The ^{13}C NMR spectrum shows that the imine carbon atoms, (165.123 ppm), are chemically equivalent in the region corresponding to the signals of aromatic ring carbons (118.298–158.474 ppm), fifteen peaks are observed as expected. The ^1H NMR spectrum of the ligand $[\text{H}_2\text{L}^2]$ shows two single ^1H imine resonances at ca. 8.409 and 8.428 ppm, supporting the non-equivalence of the two imine environments. ^{13}C NMR spectrum of this ligand shows that in the region corresponding to the signals of aromatic rings carbons (117.531–158.436 ppm) 20 peaks instead of thirty expected peaks are observed, due to high similarity of carbons and low resolution of instrument.

The ^1H NMR paramagnetic spectra of $[\text{CoL}^1]$ and $[\text{CoL}^2]$, were measured in the range from +120 to –120 ppm. The spectra of the complexes are different with those of free ligands due to their paramagnetism, which complicated spectra interpretation. It has been reported that in the NMR spectra of $\text{Co}(\text{salen})$ complexes, the most upfield shifted resonances which are usually weak and broad, can be assigned to the hydrogen in $-\text{CH}=\text{N}-$ group [39]. In the ^1H NMR spectra of present $\text{Co}(\text{II})$ complexes the latter signal was observed at –36.103 ppm for $[\text{CoL}^1]$ and –38.601 ppm and –30.976 ppm for $[\text{CoL}^2]$. Two single ^1H imine resonances for $[\text{CoL}^2]$ are due to

the non-equivalence of the two imine environments. As it can be seen in Fig. 3, most of observed hydrogen resonances in $[\text{CoL}^1]$, as expected, are doubled for corresponding asymmetric $[\text{CoL}^2]$ complex.

3.4. Electronic absorption spectroscopy

The electronic spectra of the ligands and their metal complexes were recorded in CHCl_3 . The bands below 365 nm are attributable to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the electronic spectra of the complexes, the intraligand transitions are slightly shifted as a result of coordination.

The complexes of the $\text{Co}(\text{II})$ and $\text{Cu}(\text{II})$ show the low intensity shoulders at ca. 567–692 nm, which are assigned as $d-d$ transition of the metal ions. The former bands is probably due to the $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ and $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{F})$ for $[\text{CoL}^1]$ and $[\text{CoL}^2]$ complexes transition of tetrahedral geometry [40]. All spectra of the $\text{Co}(\text{II})$ and $\text{Cu}(\text{II})$ complexes show an intense band at ca. 425–436 nm, due to charge transfer transition [41–44]. The electronic spectral details of the complexes are given in Table 5.

3.5. Molar conductivity

The molar conductivities (Λ_{M}) of the $\text{Cu}(\text{II})$ and $\text{Co}(\text{II})$ metal complexes in CH_2Cl_2 at 10^{-3} M were found to be in the range $1.8\text{--}5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. These low values indicate that all their complexes are non-electrolytes due to the absence of any counter ions in their structures [45,46]. The molar conductance values of these complexes indicate that the $[\text{H}_2\text{L}^1]$ and $[\text{H}_2\text{L}^2]$ Schiff bases are coordinated to the copper(II) and cobalt(II) ions as a doubly negatively charged anions. Therefore, it seems two phenolic OH have been deprotonated and bonded to the metal ions as oxygen anion [47].

3.6. X-ray structures

The molecular structure of $[\text{CuL}^2]$ complex is shown in Fig. 4. Selected bond distances and bond angles are listed in Table 6. The X-ray structure analysis of $[\text{CuL}^2]$ complex shows only four atoms of the donor set having considerable bonding interaction with copper(II) atom. The four-coordinate $\text{Cu}(\text{II})$ is defined by the two phenolate oxygen atoms O(1) and O(4) and the two imino nitrogen atoms N(1) and N(2) in a distorted square-planar fashion. On N_2O_2 donor set ligand, the two $\text{Cu}-\text{O}$ bonds are in *trans* configuration, the $\text{Cu}-\text{O}(1)$ and $\text{Cu}-\text{O}(4)$ distances are 1.849(2) and 1.884(2) Å. The $\text{O}(1)-\text{Cu}(1)-\text{O}(4)$ bond angle is $152.01(10)^\circ$ and two N donor atoms are also in *trans* positions with a bond angle $164.59(11)$ showing an angular deviation of 15.4° from an exact *trans* coordination [48]. The plane containing N(2), O(1), N(1) and O(4) has an r.m.s. of 0.3615 and the metal atom is displaced from this plane by 0.090 Å toward O(2). The $\text{Cu}-\text{O}(3)$ distance of 3.161 Å is too long to be considered as a bond. In contrast $\text{Cu}-\text{O}(2)$ is relatively short (2.846 Å) to be considered as a very weak coordinative bond.

It is interesting that the ligand L^2 is considerably folded, so three CH/π interactions are established (see Fig. 5). For surveying CH/π interactions in compounds bearing an arene ring, several kinds of distance and angle parameters have been defined. Fig. 6 illustrates a number of such parameters for a six-membered arene ring [49]. The corresponding values of θ , D_{lin} and D_{atm} for $[\text{CuL}^2]$ are also shown in latter figure. As can be seen the substituted *t*-butyl groups on both initial amine and aldehyde precursors are involved in CH/π interactions in resulting Schiff base complex.

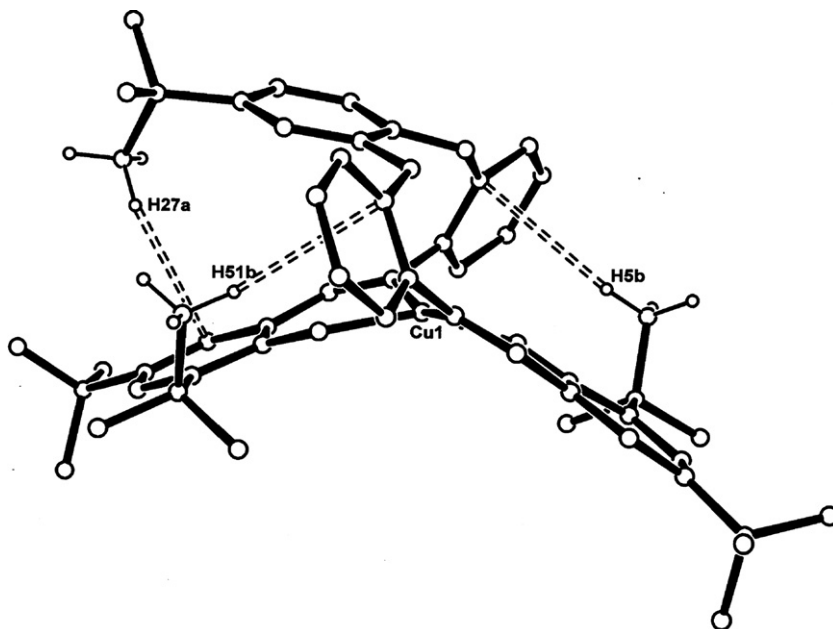


Fig. 5. Illustration of CH/π interactions in molecular structure of [CuL²]. The interactions with nearest sp² carbon atom are shown.

	D _{lin} (Å)	D _{atm} (Å)	θ (°)
H5b	3.04	3.07	20.1
H27a	3.19	3.26	43.9
H51b	2.95	3.02	17.1

Fig. 6. Some distance and angle parameters for surveying CH/π interactions. X¹ and X²: nearest and second nearest sp² atoms, respectively, to H; θ: H-C-X¹; D_{lin}: distance between H and line X¹X²; D_{atm}: interatomic distance (H/X¹).

4. Conclusion

We report here a study of the coordination capability of two new potentially hexadentate N₂O₄ Schiff base ligands [H₂L¹] and [H₂L²] towards Cu(II) and Co(II). It was found that due to the rigidity of the ligands and/or sizes of the present metal ions, only N₂O₂ donor set having bonding interaction. The ligand L² is considerably folded, so three CH/π interactions are established through substituted *t*-butyl groups with arene rings.

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Appendix A. Supplementary material

CCDC 669000 contains the supplementary crystallographic data for [CuL²]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article

can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.07.012](https://doi.org/10.1016/j.jorganchem.2008.07.012).

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