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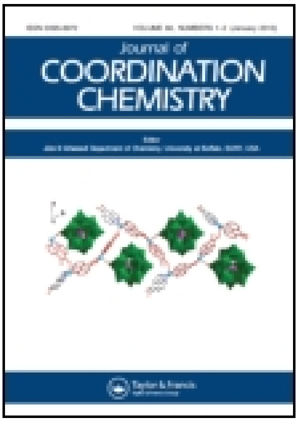

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Synthesis, characterization, and crystal structures of cobalt(II), copper(II), and zinc(II) complexes of a bidentate iminophenol

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Synthesis, characterization, and crystal structures of cobalt(II), copper(II), and zinc(II) complexes of a bidentate iminophenol

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A bidentate iminophenol (HL = 2-((4-methoxyphenylimino)methyl)-4,6-di-*tert*-butylphenol derived from condensation of 4-methoxyaniline and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde) was mixed with divalent metal salts to form the corresponding mononuclear metal complexes $[M^{II}(L)_2]$ (M = Co (**1**), Cu (**2**), and Zn (**3**)). The complexes are characterized by different spectroscopic and analytical tools. X-ray crystal structures of the complexes revealed homoleptic mononuclear complexes with MN_2O_2 coordination. The cobalt(II) (**1**) and zinc(II) (**3**) complexes display a *pseudo*-tetrahedral coordination geometry, whereas the copper(II) complex (**2**) exhibits a distorted square-planar coordination. The zinc(II) complex (**3**) emits at 460 nm with a twofold enhancement of emission with respect to the free iminophenol.

Keywords: Iminophenol; Transition metal complexes; Crystal structure; Fluorescence; Zinc

1. Introduction

Coordination chemistry of transition metal complexes of iminophenol ligands derived from Schiff-base condensation has been extensively studied over the last few decades [1–8]. Versatile binding motifs of iminophenols with transition metal ions have been documented [9–13]. Transition metal complexes of iminophenols derived from substituted aniline and salicylaldehyde have been structurally characterized and used to study phenol oxidation, antibacterial, and antifungal activity [14–18]. Zinc complexes of iminophenols are photoluminescent and iminophenols are widely used as zinc(II) selective sensors [6, 19–25]. Recently we reported a series of binuclear metal complexes of bis(bidentate) iminophenols [25, 26]; only the zinc complexes of the asymmetric ditopic ligands have been shown to exhibit photoluminescence [25]. The majority of the zinc complexes reported are polynuclear clusters and the iminophenols are multidentate. Although, a few reports on mononuclear zinc complexes with simple bidentate iminophenol are found, they exhibit poor emission [15, 22, 27, 28]. It is therefore important to design new bidentate iminophenols which upon binding to Zn^{2+} would show selective fluorescence with better quantum yield.

We have developed a bidentate iminophenol derived from the Schiff-base condensation of *p*-methoxyaniline and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde. A series of transition

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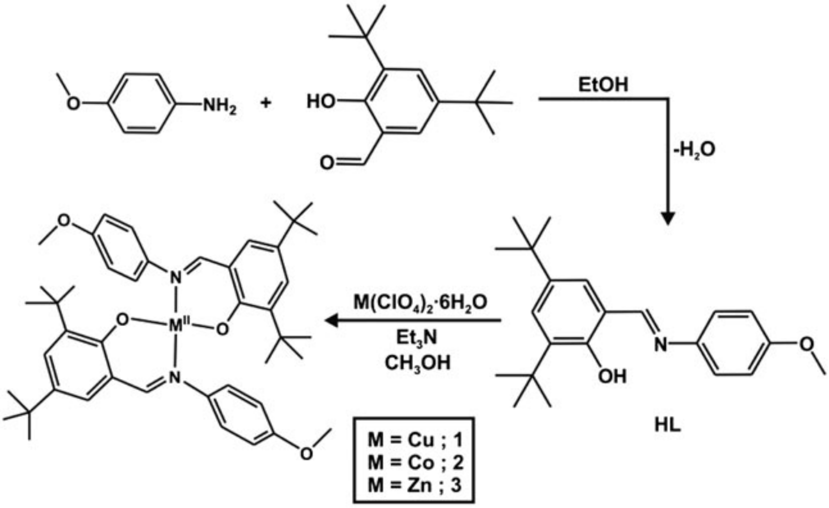

Scheme 1. Synthesis of the iminophenol (HL) and the complexes.

metal complexes of the ligand have been isolated to study their emission behavior. Zinc complex of an analogous iminophenol synthesized by Schiff-base condensation of *p*-methoxyaniline and salicylaldehyde has been structurally characterized and shows emission with low quantum yield [13, 20]. The effect of *tert*-butyl substitution on salicylaldehyde ring on the geometry at the metal centers and the emission behavior of the transition metal complexes have been studied.

In this article, we report the synthesis, characterization, and photophysical studies of three mononuclear transition metal complexes with general formula $[M^{II}(L)_2]$ (M = Co, Cu, and Zn) of a bidentate iminophenol, 2-((4-methoxyphenylimino)methyl)-4,6-di-*tert*-butylphenol (HL), derived from Schiff-base condensation of *p*-methoxyaniline and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (scheme 1).

2. Experimental

2.1. *General considerations and physical methods*

Commercial grade chemicals were used for syntheses. Solvents were distilled and dried prior to use. *Although no problem was encountered during the synthesis of the complexes, perchlorate salts are potentially explosive and should be handled with care!* [29].

Fourier transform infrared spectroscopy of KBr pellets was performed on a Shimadzu FT-IR 8400S instrument. Elemental analyzes were performed on a Perkin Elmer 2400 series II CHN analyzer. Electrospray mass spectra were recorded with a Waters QTOF Micro YA263. ^{1}H NMR spectra were measured at room temperature on Bruker DPX-300 and 500 MHz spectrometers. Room temperature electronic spectra were recorded on an Agilent 8453 Diode Array Spectrophotometer from 190 to 1100 nm. Electronic spectra of the ligands and complexes were measured in DMSO at ambient conditions using a cell with path length 1 cm. Luminescence spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer. Emission spectra of the ligands and complexes were recorded in DMSO at ambient conditions with excitation slit width 10 nm, emission slit width 5 nm, and scan speed 200 nm min^{-1}. Anthracene was used as a reference fluorescence dye for HL and quininebisulphate monohydrate as reference for complexes for the measurement of quantum yield [30]. Room temperature magnetic data were collected on a Gouy balance (Sherwood Scientific, Cambridge, UK). Diamagnetic contributions were estimated for each compound by using Pascal's constants.

2.2. *Synthesis of HL*

To a solution of 4-methoxy aniline (0.25 g, 2 mmol) in 10 mL ethanol, a solution (10 mL) of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.46 g, 2 mmol) in ethanol was added dropwise. A yellow crystalline solid separated slowly upon stirring. The resulting mixture was stirred for 6 h and the solid was isolated by filtration. The solid was further recrystallized from dichloromethane–methanol.

Yield: 75% (0.51 g). Anal. Calcd for $C_{22}H_{29}NO_2$ (339.47 g mol^{-1}): C, 77.84; H, 8.61; N, 4.13. Found: C, 77.9; H, 8.4; N, 4.0%. IR (KBr, cm^{-1}): 3462(br), 2959–2868(s), 1616(s), 1506(s), 1467(s), 1423(m), 1361(m), 1298(m), 1246(s), 1170(s), 1034(s), 827(m). ESI-MS (positive ion mode, CH_2Cl_2): *m/z* = 340.22 (100%, $[L^1 + H]^+$). ^{1}H NMR (300 MHz, DMSO-d_6): δ, ppm: 14.05 (s, 1H), 8.95 (s, 1H), 7.43 (m, 4H), 7.01 (d, 2H, J = 9 Hz), 3.79 (s, 3H), 1.41 (s, 9H), 1.29 (s, 9H). UV-vis in DMSO (λ): 358 nm (ε = 17,110 M^{-1} cm^{-1}), 332 nm (ε = 20,100 M^{-1} cm^{-1}).

2.3. *General method for the synthesis of 1–3*

To a solution of metal(II) perchlorate hexahydrate (0.5 mmol) in 10 mL methanol, a methanolic solution (10 mL) of HL (1 mmol) was added and followed by the addition of Et_3N (140 µL, 1 mmol). The reaction mixture was stirred at room temperature for 5 h to precipitate a solid. The solid was isolated by filtration and air-dried. Single crystals suitable for X-ray diffraction were grown from a concentrated CH_2Cl_2–CH_3OH solution of the complex.

2.3.1. $[Co^{II}(L)_2]$ (1). Red solid: Yield: 69% (0.25 g). Anal. Calcd for $C_{44}H_{56}N_2O_4Co$: C, 71.82; H, 7.67; N, 3.81. Found: C, 70.8; H, 7.6; N, 3.9%. IR (KBr, in cm^{-1}): 2955, 2906, 2868(s), 1612(s), 1579(s), 1527(m), 1506(s), 1462(m), 1421(s), 1385(m), 1250(s), 1167(s), 1034(m), 835(m), 785(m), 538(w), 496(w). ESI-MS (positive ion mode, CH_2Cl_2): *m/z* = 340.27 (100%, $[L + H]^+$), 736.15 (30%, $[Co(L)_2 + H]^+$). UV-vis in DMSO (λ): 425 nm (ε = 8700 M^{-1} cm^{-1}), 370 nm (ε = 16,900 M^{-1} cm^{-1}), 312 nm (ε = 25,000 M^{-1} cm^{-1}). μ_{eff} (298 K): 4.07 μ_B.

2.3.2. $[Cu^{II}(L)_2]$ (2). Brown solid: Yield: 73% (0.27 g). Anal. Calcd for $C_{44}H_{56}N_2O_4Cu$: C, 71.37; H, 7.62; N, 3.78. Found: C, 71.2; H, 7.6; N, 3.7%. IR (KBr, in cm^{-1}): 2957, 2905, 2868(s), 1614(s), 1591(s), 1529(m), 1504(s), 1460(m), 1427(s), 1385(m), 1252(s), 1167(s), 1034(m), 831(m), 748(m), 532(m), 496(m). ESI-MS (positive ion mode, CH_2Cl_2): *m/z* = 340.32 (100%, $[L + H]^+$), 740.27 (30%, $[Cu(L)_2 + H]^+$). UV-vis in DMSO(λ): 405 nm (ε = 15,000 M^{-1} cm^{-1}), 302 nm (ε = 32,000 M^{-1} cm^{-1}). μ_{eff} (298 K): 1.70 μ_B.

2.3.3. [Zn^{II}(L)$_2$] (3). Yellow solid: Yield: 78% (0.26 g). Anal. Calcd for $C_{44}H_{56}N_2O_4Zn$: C, 71.19; H, 7.60; N, 3.77. Found: C, 71.2; H, 7.4; N, 4.0%. IR (KBr, in cm^{-1}): 2957(s), 1612(s), 1585(s), 1529(m), 1506(s), 1460(m), 1427(s), 1391(m), 1252(s), 1165(s), 1034(m), 835(m), 785(m), 532(m), 495(w). ESI-MS (positive ion mode, CH_2Cl_2): m/z = 340.37 (100%, $[L + H]^+$), 741.66 (20%, $[Zn(L)_2 + H]^+$). ^1H NMR (300 MHz, DMSO-d$_6$): δ, ppm: 8.74 (s, 2H), 7.38 (s, 2H) 7.32 (s, 2H), 7.24 (d, 4H, J = 9 Hz), 6.87 (d, 4H, J = 9 Hz), 3.69 (s, 6H), 1.33 (s, 18H), 1.27 (s, 18H). UV-vis in DMSO (λ) : 420 nm (ε = 8000 M^{-1} cm^{-1}), 358 nm (ε = 26,900 M^{-1} cm^{-1}), 330 nm (ε = 34,100 M^{-1} cm^{-1}).

2.4. *X-ray crystallographic data collection and refinement of the structures*

Crystallographic data of HL, **1**, **2**, and **3** are given in table 1. Diffraction data were collected at 120 K on a Bruker Smart APEX II (Mo-Kα radiation, λ = 0.71073 Å). Cell refinement, indexing, and scaling of the data-set were carried out using the APEX2 v2.1–0 software [31]. The structures were solved by direct methods and subsequent Fourier analyzes and refined by full-matrix least-squares based on F^2 with all observed reflections [32]. All non-hydrogen atoms were refined anisotropically and hydrogens were fixed.

3. Results and discussion

3.1. *Isolation and spectroscopic characterization*

The iminophenol, 2-((4-methoxyphenylimino)methyl)-4,6-di-*tert*-butylphenol (HL), was prepared by Schiff-base condensation of *p*-methoxyaniline and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (scheme 1). The complexes were synthesized by mixing HL, metal(II) perchlorate hexahydrate, and triethylamine in methanol (scheme 1). The iminophenol and the complexes were characterized by different spectroscopic and analytical tools. IR spectrum of the iminophenol displays a phenolic –OH stretch at 3460 cm^{-1} which is absent in the metal complexes. The iminophenol also exhibits a sharp band at 1616 cm^{-1} which is attributed to stretch of imine (–C=N). The stretch of the imine appears at lower frequency in all the complexes. The M–N stretch is observed at 532–538 cm^{-1} and a weak band, attributable to ν(M–O) stretch, appears at 495 cm^{-1}. All these data suggest coordination of iminophenolate with the metal through the imine nitrogen and phenolate oxygen. Elemental analyzes of the complexes suggest formation of neutral complexes with a common molecular composition, $C_{44}H_{56}N_2O_4M$, where the metal to ligand ratio is 1 : 2. The molecular ion peaks at m/z = 736.15, 740.27, and 741.66 with the isotopic distribution patterns calculated for $[Co(L)_2 + H]^+$, $[Cu(L)_2 + H]^+$, and $[Zn(L)_2 + H]^+$ are observed in the ESI-MS spectra of **1**, **2**, and **3**, respectively. The optical spectrum of iminophenol shows π–π* transitions at 330 and 358 nm whereas the charge-transfer transition is observed at 422, 405, and 420 nm for **1**, **2**, and **3**, respectively. The cobalt and copper complexes (**1** and **2**) exhibit effective magnetic moments of 4.02 and 1.70 μ_B, respectively, at room temperature. The room temperature magnetic moments of the complexes are indicative of high-spin cobalt(II) and copper(II), respectively.

3.2. *^{1}H NMR spectra*

The free ligand shows proton resonances from 0 to 15 ppm. A sharp singlet is observed at 14.0 ppm assigned as the phenolic –OH resonance. The proton attached with the imine

Table 1. Crystallographic information for HL, **1**, **2**, and **3**.

Parameters	HL	**1**	**2**	**3**
Empirical formula	$C_{22}H_{29}NO_2$	$C_{44}H_{56}N_2O_4Co$	$C_{44}H_{56}N_2O_4Cu$	$C_{44}H_{56}N_2O_4Zn$
Formula weight	339.46	735.84	740.45	742.28
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P_2(1)/c$	$P_2(1)/c$	$P{-}1$	$P_2(1)/c$
a, Å	18.421(6)	18.052(3)	10.7710(5)	17.7817(10)
b, Å	10.324(3)	18.238(3)	14.4113(7)	17.9871(10)
c, Å	10.622(4)	13.363(2)	14.6104(7)	13.3430(8)
α, °	90.00	90.00	78.8830(10)	90.00
β, °	95.027(10)	105.528(4)	71.4640(10)	105.7040(10)
γ, °	90.00	90.00	89.4760(10)	90.00
Volume, Å^3	2012.2(11)	4239.1(11)	2106.57(17)	4108.3(4)
Z	4	4	2	4
D_{Calcd} Mg m^{-3}	1.121	1.153	1.167	1.200
μ Mo Kα, mm^{-1}	0.071	0.445	0.559	0.640
F (000)	736	1572	790	1584
θ Range, °	1.11–25.00	1.17–21.64	1.44–25.00	1.19–27.50
Reflections collected	23,207	27,900	25,013	44,661
Reflns. unique	3542	4926	7376	9321
R(int)	0.0221	0.1125	0.0229	0.0376
Data ($I > 2\sigma(I)$)	2888	3110	6456	7419
Parameters refined	234	474	474	474
Goodness-of-fit on F^2	1.029	0.932	1.047	0.926
$R1$ [$I > 2\sigma(\mathrm{I})$]	0.0642	0.0559	0.0403	0.0349
w$R2$	0.1968	0.1385	0.1210	0.1074
Residuals e Å^{-3}	0.581, −0.237	0.218, −0.363	0.562, −0.515	0.565, −0.289

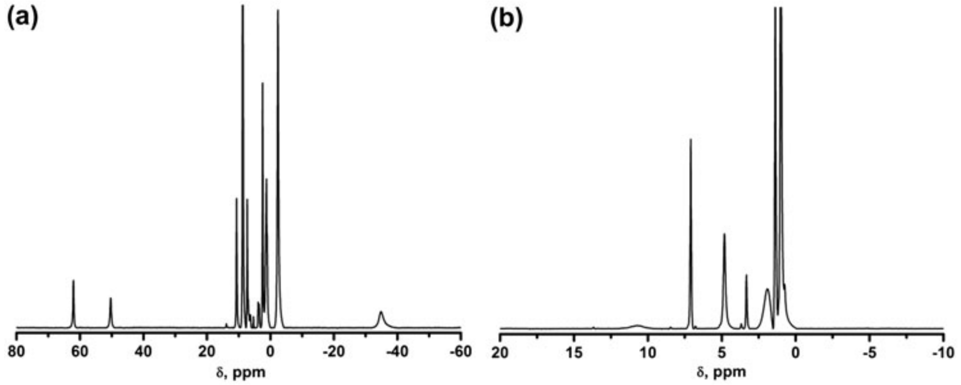

Figure 1. ^{1}H NMR spectra of **1** and **2** in $CDCl_3$ in 500 MHz at 298 K.

(–CH=N–) shifts downfield to 8.95 ppm as a sharp singlet. The *meta*-protons of phenyl are observed at 7.01 ppm as doublets with a coupling constant of 9 Hz. The multiplets at 7.43 ppm are assigned as the resonance of the rest of the aromatic protons of salicylaldehyde and *p*-methoxyaniline. The number of peaks observed for **3** suggests that the complex has twofold symmetry in solution. In the ^{1}H NMR spectrum of **3**, the proton resonance of

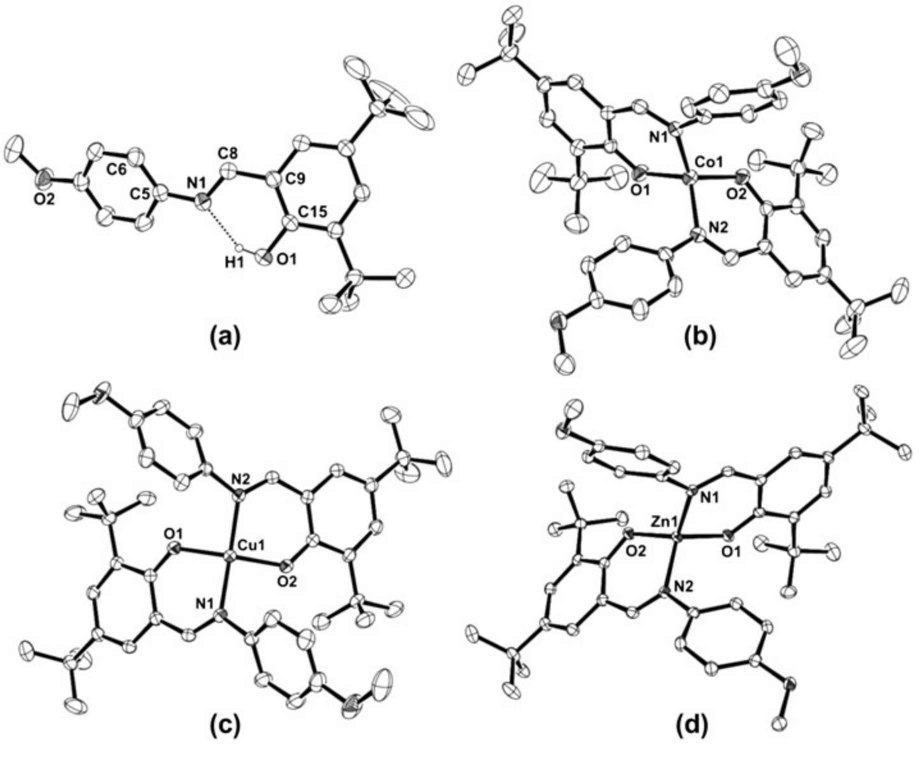

Figure 2. ORTEP plots of (a) HL, (b) **1**, (c) **2** and (d) **3** with 30% thermal ellipsoid probability.

phenolic –OH is absent and the imine proton is shifted upfield by 0.2 ppm. Aromatic protons of the phenolate ring of the ligand are singlets at 7.38 and 7.32 ppm, respectively. Two doublet peaks are found at 7.24 and 6.87 ppm with coupling constant of 9 Hz suggesting aromatic protons of phenyl. The proton resonances of iminophenol are upfield shifted upon complexation with zinc(II). A comparison of the proton resonances of free HL with **3** suggests binding of iminophenolate with Zn^{2+} as evident from ^1H NMR spectra (Supplementary material).

While the zinc complex (**3**) is diamagnetic, the cobalt(II) and copper(II) complexes are paramagnetically shifted. The ^1H NMR spectrum of **1** in $CDCl_3$ exhibits resonances from −40 to 70 ppm, whereas **2** shows resonances from 0 to 15 ppm (figure 1). The upfield peaks are broad and can be assigned as protons of the ligand, close to the metal center. It is difficult to assign all the peaks in the ^1H NMR spectra of **1** and **2**, but the spectra are indicative of binding of the iminophenol to paramagnetic Co^{2+} and Cu^{2+}.

3.3. *X-ray crystal structure*

X-ray diffraction quality single crystals of HL were grown from a solvent mixture of dichloromethane and methanol. The iminophenol crystallizes monoclinic with $P2_1/c$ space group. The asymmetric unit consists of one iminophenol with C8–N1 distances of 1.270(3) Å (figure 2(a)). A strong intramolecular hydrogen bond with phenolate oxygen (O1) and imine nitrogen (N1) at 2.584 Å makes the phenol ring coplanar with imine bond (C8–N1). However, solid state packing of the molecule allows the 4-methoxy-phenyl ring to deviate from the iminophenolato ring with dihedral angle of 31.82°. The selected bond distances and angles are listed in table 2.

X-ray diffraction of single crystals of **1**–**3** was performed to know the binding motif of the iminophenol. The solid state structures reveal formation of neutral four-coordinate mononuclear complexes (figure 2(b–d)). In each complex, the metal ion is ligated through two imine nitrogens and two phenolate oxygens of the monoanionic iminophenolate. The geometry is pseudo-tetrahedral in **1** and **3**, but distorted square planar in **2**. However, a comparable bite angle (O1–M–N1 and O2–M–N2) of the bidentate iminophenolate is observed in the three complexes (table 3). The $M–O_{phenolate}$ and $M–N_{imine}$ distances are comparable with the previously reported transition metal complexes of iminophenols [15–17, 25, 26, 28].

3.4. *Fluorescence*

The iminophenol exhibits a weak emission at 420 nm (Φ_F = 0.040) upon excitation at 358 nm. While cobalt (II) and copper(II) complexes do not show appreciable emission, zinc (II) complex emits at 460 nm (Φ_F = 0.088) upon excitation with 415 nm with a twofold enhancement of fluorescence intensity with respect to the free iminophenol (figure 3). The

Table 2. Selected bond lengths (Å) and angles (°) for HL.

C(15)–O(1)	1.346(2)	C(5)–N(1)	1.421(3)
C(8)–N(1)	1.270(3)	O(1)–C(15)–C(14)	119.97(19)
O(1)–C(15)–C(9)	119.71(19)	C(9)–C(8)–N(1)	122.1(2)
N(1)–C(5)–C(6)	125.0(2)	N(1)–C(5)–C(4)	116.7(2)
C(8)–N(1)–C(5)	121.4(2)		

Table 3. Selected bond lengths (Å) and angles (°) of **1–3**.

	1	**2**	**3**
M(1)–O(1)	1.892(4)	1.892(1)	1.904(1)
M(1)–O(2)	1.889(3)	1.887(2)	1.912(1)
M(1)–N(1)	1.980(4)	1.966(2)	2.004(1)
M(1)–N(2)	1.987(4)	1.970(2)	1.996(1)
O(1)–M(1)–N(1)	94.31(16)	93.25(7)	96.89(5)
O(1)–M(1)–N(2)	113.68(16)	91.92(7)	119.86(6)
O(2)–M(1)–N(2)	96.35(16)	92.91(7)	94.81(6)
O(2)–M(1)–N(1)	119.11(16)	92.06(7)	113.15(6)
O(1)–M(1)–O(2)	119.42(16)	152.19(9)	118.06(6)
N(1)–M(1)–N(2)	115.45(17)	158.77(8)	115.40(6)

complex shows emission at the same position upon excitation with other wavelengths and the highest quantum yield was obtained upon excitation with 415 nm. The mononuclear zinc complex of 2-((4-methoxyphenylimino)methyl)phenol, an analogous iminophenol of HL, exhibits emission at 480 nm with a low quantum yield of 0.011 [22]. Thus, the comparison with analogous system clearly demonstrates that incorporation of *tert*-butyl groups into the phenolate ring leads to a 20 nm blueshift in emission with intensity enhanced ninefold. Similarly, a twofold enhancement is found among the zinc complexes of the iminophenols derived from the condensation of 4-aminobenzylamine with salicylaldehyde and 3,5-di-*tert*-butyl-salicylaldehyde [25]. Enhancement of electron density on the phenol ring results in an increment in emission. A single crystal of **3** appears green when

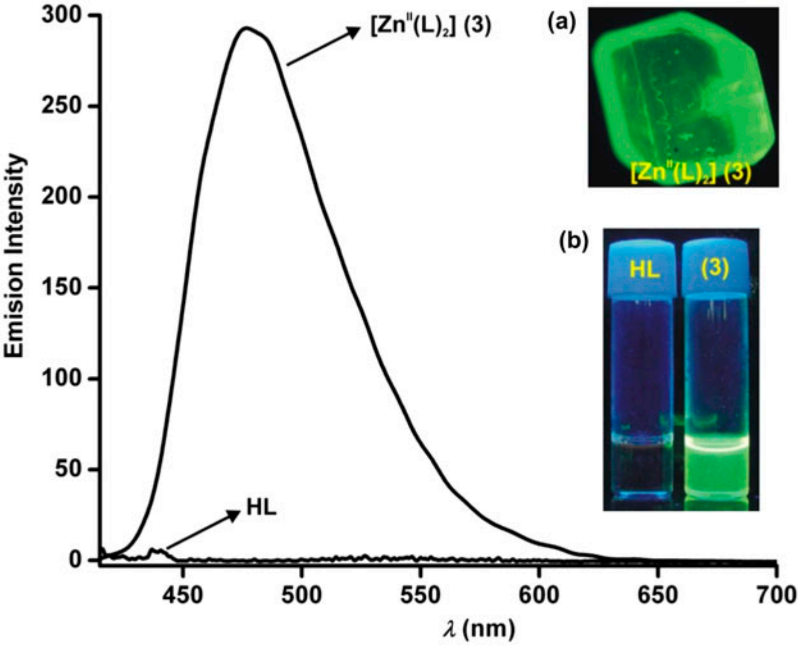

Figure 3. Emission spectra of iminophenol (HL) and **3** in DMSO (conc. 1 μM). λ_{ex} = 360 nm for HL, λ_{ex} = 415 nm for **3**. (a) A single crystal of **3** viewed under fluorescence microscope in visible light. (b) The solution of HL and **3** in DMSO under UV light.

viewed under a fluorescence microscope in visible light (figure 3(a)). Solution of the zinc complex is distinct fluorescent green in DMSO under UV light, whereas solutions of HL, cobalt, and copper complexes do not show any observable color (figure 3(b)). Thus, zinc complex of HL is luminescent in both solid state and solution, and the iminophenol is capable of showing zinc-selective fluorescence.

4. Conclusions

Neutral complexes (cobalt(II), copper(II), and zinc(II)) of a bidentate iminophenol (HL) have been synthesized and characterized. In all the homoleptic bis-complexes, the metal ion is coordinated through the imine nitrogen and the phenolate oxygen of a monoanionic iminophenolate. The cobalt(II) and copper(II) complexes are paramagnetic, whereas the zinc(II) complex is diamagnetic. Only the zinc(II) complex shows emission in both solid state and in solution. A twofold enhancement of emission is observed with respect to the free iminophenol. The iminophenol shows zinc-selective fluorescence. A comparative study with analogous complexes suggests that incorporation of *tert*-butyl on phenolate ring results in an enhanced emission. We are trying to develop other iminophenols soluble in water which could be applicable for zinc(II) sensing in biological samples.

Supplementary material

CCDC-932035 (for HL), -932036 (for **1**), -932037 (for **2**), and -932038 (for **3**) contain the supplementary crystallographic data of the crystal structure of this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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References

[1] S. Yamada. *Coord. Chem. Rev.*, **190**, 537 (1999).
[2] C. Demetgul, M. Karakaplan, S. Serin, M. Digrak. *J. Coord. Chem.*, **62**, 3544 (2009).
[3] M.K. Singh, N.K. Kar, R.A. Lal, M. Asthana. *J. Coord. Chem.*, **62**, 2893 (2009).
[4] N. Raman, S. Johnson Raja, A. Sakthivel. *J. Coord. Chem.*, **62**, 691 (2009).
[5] A.D. Garnovskii, I.S. Vasilchenko, D.A. Garnovskii, B.I. Kharisov. *J. Coord. Chem.*, **62**, 151 (2009).
[6] A. Patra, S. Sarkar, R. Chakraborty, M.G.B. Drew, P. Chattopadhyay. *J. Coord. Chem.*, **63**, 1913 (2010).
[7] R.C. Maurya, P. Patel, S. Rajput. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 817 (2003).

[8] S.H. Alarcon, A.C. Olivieri, A. Nordon, R.K. Harris. *J. Chem. Soc., Perkin Trans.*, **2**, 2293 (1996).
[9] A.D. Garnovaskii, A.L. Nivorozhkin, V.I. Minkin. *Coord. Chem. Rev.*, **126**, 1 (1993).
[10] A. Syamal, M.R. Maurya. *Coord. Chem. Rev.*, **95**, 183 (1989).
[11] H. Houjou, M. Ito, K. Araki. *Inorg. Chem.*, **48**, 10703 (2009).
[12] D.V. Baxter, K.G. Caulton, W.-C. Chiang, M.H. Chisholm, V.F. DiStasi, S.G. Dutremez, K. Folting. *Polyhedron*, **20**, 2589 (2001).
[13] A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra. *Polyhedron*, **25**, 1753 (2006).
[14] G.G. Mohamed, M.M. Omar, A.M. Hindy. *Turk. J. Chem.*, **30**, 361 (2006).
[15] L. Tatar, D. Ulku, O. Atakol. *Acta Cryst.*, **C55**, 508 (1999).
[16] J.L. van Wyk, S.F. Mapolie, A. Lennartson, M. Hakansson, S. Jagner. *Inorg. Chim. Acta*, **361**, 2094 (2008).
[17] R. Vafazadeh, V. Hayeri, A.C. Willis. *Polyhedron*, **29**, 1810 (2010).
[18] W. Rehman, F. Saman, I. Ahmad. *Russ. J. Inorg. Chem.*, **34**, 678 (2008).
[19] P. Jiang, Z. Guo. *Coord. Chem. Rev.*, **248**, 205 (2004).
[20] P. Roy, K. Dhara, M. Manassero, J. Ratha, P. Banerjee. *Inorg. Chem.*, **46**, 6405 (2007).
[21] U.C. Saha, B. Chattopadhyay, K. Dhara, S.K. Mandal, S. Sarkar, A.R. Khuda-Bukhsh, M. Mukherjee, M. Helliwell, P. Chattopadhyay. *Inorg. Chem.*, **50**, 1213 (2011).
[22] L. Chen, J. Qiao, J. Xie, L. Duan, D. Zhang, L. Wang, Y. Qiu. *Inorg. Chim. Acta*, **362**, 2327 (2009).
[23] S. Range, D.F.-J. Piesik, S. Harder. *Eur. J. Inorg. Chem.*, 3442 (2008).
[24] J. Domer, J.C. Slootweg, F. Hupka, K. Lammertsma, F.E. Hahn. *Angew. Chem. Int. Ed.*, **49**, 6430 (2010).
[25] B. Chakraborty, P. Halder, S. Chakraborty, O. Das, S. Paria. *Inorg. Chim. Acta*, **387**, 332 (2012).
[26] P. Halder, P.R. Banerjee, E. Zangrando, T.K. Paine. *Eur. J. Inorg. Chem.*, 5659 (2008).
[27] N. Raman, V. Muthuraj, S. Ravichandran, S. Kulandaisamy. *Proc. Indian Acad. Sci.* (*Chem. Sci.*), **115**, 161 (2003).
[28] R.L. De, M. Mandal, L. Roy, J. Mukherjee, R. Bhawal, K. Maiti. *Indian J. Chem.*, **47A**, 1480 (2008).
[29] W.C. Wolsey. *J. Chem. Educ.*, **50**, A335 (1973).
[30] D.F. Eaton. *Pure Appl. Chem.*, **60**, 1107 (1988).
[31] Bruker. *APEX 2*, Bruker AXS Inc., Madison, Wiskonsin, USA (2006).
[32] G.M. Sheldrick. *SHELX97 Programs for Crystal Structure Analysis (Release 97–2)*, University of Göttingen, Germany (1998).