Inorganica Chimica Acta 387 (2012) 332–337

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, characterization and emission study of zinc(II) and cobalt(II) complexes: Bis(bidentate) iminophenols as zinc(II) selective fluorescence probes

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ARTICLE INFO

Article history:
Received 2 December 2011
Received in revised form 7 February 2012
Accepted 15 February 2012
Available online 23 February 2012

Keywords:
Iminophenol
Zinc
Fluorescence
Cobalt
Solid state structures

ABSTRACT

Two zinc(II) complexes, $[Zn^{II}_2(L^1)_2]$ (**1**) and $[Zn^{II}_2(L^2)_2]$ (**2**), and two cobalt(II) complexes, $[Co^{II}_2(L^1)_2]$ (**3**) and $[Co^{II}_2(L^2)_2]$ (**4**), (H_2L^1 = iminophenol derived from the condensation of 4-aminobenzylamine and salicyldehyde, H_2L^2 = Schiff-base of 4-aminobenzylamine and 3,5-di-*tert*-butylsalicyldehyde) supported by bis(N,O-bidentate) ligands have been synthesized and characterized. X-ray single crystal structures of **3** and **4** revealed the dimeric nature of the complexes with a 1:1 ratio of metal and ligand. The zinc(II) complexes have a very similar composition as established from different analytical and spectroscopic techniques. The iminophenols exhibit highly selective fluorescence enhancement with high quantum yield upon binding with Zn^{2+} in solution. A 50-fold enhancement of emission in zinc(II) complexes is observed with respect to free iminophenols.

1. Introduction

Zinc, the second most abundant metal ion in human body after iron, is involved in several major biological functions including enzyme regulation, gene transcription and neural signal transmission and in Alzheimer disease [1–14]. Zn^{2+} is present in the active site of many non-redox metalloenzymes like carbonic anhydrase, carboxypeptidase, liver alcohol dehydrogenase, etc [15–17]. Detection of Zn^{2+} in biological system is quite challenging due to its lack of spectroscopic signature of the closed-shell electronic configuration and for its low concentration in many biological samples [18]. Additionally, detection of Zn^{2+} in the presence of Cd^{2+} is difficult because they have similar chemical properties [19–23]. To overcome this problem, the design of simple synthetic probe which can selectively detect Zn^{2+} in low concentration is of particular interest. Several Zn^{2+} selective fluorescent probes are now commercially available [24–26]. Zinc(II) selective sensors based on 8-aminoquinoline, 8-hydroxyquinoline or other fluorescent derivatives have been reported in the literature [27–34]. Every system has its own advantages and disadvantages. Therefore, searches are still on for the development of simple sensors with high selectivity, sensitivity and reliability. In this direction, several Schiff-base fluorescent probes that are easy to synthesize have been developed [33–39]. We have been working with Schiff-base ligands derived from the condensation of 4-aminobenzylamine and salicyldehyde derivatives (Scheme 1). Recently, we have reported a dinuclear copper(II) complex of H_2L^2 with head–head or tail–tail combination of the asymmetric ditopic ligand [40]. Several metal complexes of H_2L^1 have been reported without any structural characterization [41]. Zinc(II) complexes of bis(bidentate) iminophenol ligands are also known [42–44]. However, the ability of the iminophenols as fluorescence probes has not been documented.

We report in this paper the selective and sensitive fluorescence sensing of Zn^{2+} ion using two bis(bidentate) iminophenols (Scheme 1). The synthesis and characterization of two zinc(II) and two cobalt(II) complexes are described.

2. Experimental

2.1. General considerations and physical methods

All chemicals were purchased from commercial sources and used as received. Solvents were distilled and dried before use. Although no problem was encountered during the synthesis of the complexes, perchlorate salts are potentially explosive and should be handled with care [45]. Ligands were synthesized according to the reported procedure [40,41].

Fourier transform infrared spectroscopy on KBr pellets was performed on a Shimadzu FT-IR 8400S instrument. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. Electro-spray mass spectra were recorded with a Waters QTOF Micro YA263. ^1H NMR spectra were measured at room temperature on Bruker DPX-300 spectrometer. Room temperature electronic spectra were recorded on an Agilent 8453 Diode Array

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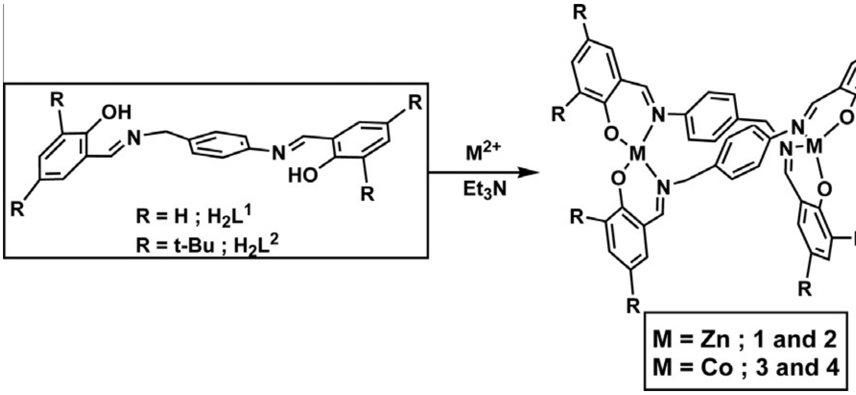
doi:10.1016/j.ica.2012.02.024



Scheme 1. Synthesis of complexes.

spectrophotometer over 190–1100 nm scan range. Luminescence spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer. Quantum yield was calculated according to the reported procedure and quinine bisulfate was used as the reference standard [46]. 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. General method for the synthesis of complexes

To an acetonitrile solution of 10 mL of metal perchlorate (1 mmol), ligand (1 mmol) and triethylamine (2 mmol) were added. The resulting solution was stirred for 24 h to precipitate a solid. The solid was separated by filtration and dried in air. The solid was recrystallized from a solvent mixture of dichloromethane and acetonitrile.

2.2.1. $[Zn^{II}_2(L^1)_2]$ (**1**)

Yield: 75%, 0.59 g. *Anal.* Calc. for $C_{42}H_{32}N_4O_4Zn_2$: C, 64.06; H, 4.10; N, 7.11. Found: C, 64.01; H, 4.31; N, 6.93%. IR (KBr, in cm^{-1}) 3427 (br), 1620 (s), 1583 (s), 1533 (m), 1464 (m), 1443 (s), 1392 (m), 1317 (m), 1178 (m), 1149 (m), 760 (m). ^1H NMR (300 MHz, $CDCl_3$): δ, ppm: 8.43 (s, 1H), 8.35 (s, 1H) 7.37 (m, 2H), 7.18 (d, 4H, J = 6 Hz), 6.93 (t, 3H, J = 6 Hz), 6.85 (d, 3H, J = 9 Hz), 6.75 (m, 1H), 4.93 (d, 1H, J = 12 Hz) 4.38 (d, 1H, J = 12 Hz). UV–Vis in CH_2Cl_2: 404 nm (ε = 27600 M^{-1} cm^{-1}), 307 nm (ε = 29800 M^{-1} cm^{-1}).

2.2.2. $[Zn^{II}_2(L^2)_2]$ (**2**)

Yield: 81%, 0.50 g. *Anal.* Calc. for $C_{74}H_{96}N_4O_4Zn_2$: C, 71.89; H, 7.83; N, 4.53. Found: C, 71.82; H, 7.68; N, 4.50%. IR (KBr, in cm^{-1}): 3443 (br), 2957 (s), 2868 (m), 1614 (s), 1583 (s), 1526 (m), 1456 (m), 1427 (s), 1392 (m), 1257 (m), 1165 (s). ^1H NMR (300 MHz, $CDCl_3$): δ, ppm: 8.46 (s, 1H), 8.33 (s, 1H) 7.52 (m, 2H), 7.02 (m, 2H), 6.88 (s, 4H,), 4.74 (d, 1H, J = 12 Hz) 4.32 (d, 1H, J = 12 Hz). UV–Vis in CH_2Cl_2: 422 nm (ε = 17600 M^{-1} cm^{-1}), 314 nm (ε = 41100 M^{-1} cm^{-1}).

2.2.3. $[Co^{II}_2(L^1)_2]$ (**3**)

Yield: 65%, 0.25 g. *Anal.* Calc. for $C_{42}H_{32}N_4O_4Co_2$: C, 65.12; H, 4.16; N, 7.23. Found: C, 64.97; H, 4.23; N, 7.16%. IR (KBr, in cm^{-1}): 3408 (br), 1608 (s), 1578 (s), 1531 (s), 1462 (m), 1437 (s), 1313 (m), 1178 (m), 1149 (m), 760 (m). UV–Vis in CH_2Cl_2: 398 nm (ε = 23150 M^{-1} cm^{-1}), 301 nm (ε = 35350 M^{-1} cm^{-1}). μ_{eff} = 5.96 μ_B.

Table 1
Crystallographic information table for H_2L^1, H_2L^2, **3** and **4**.

Parameters	H_2L^1	H_2L^2	**3**·CH_2Cl_2	**4**·[3(CH_2Cl_2)(OH_2)]
Empirical formula	$C_{21}H_{18}N_2O_2$	$C_{37}H_{50}N_2O_2$	$C_{43}H_{34}Cl_2Co_2N_4O_4$	$C_{151}H_{200}C_{l6}Co_4N_8O_9$
Formula weight	330.37	554.79	859.50	2719.61
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	16.9236(16)	9.4306(12)	10.4164(12)	14.0173(15)
b (Å)	5.4099(5)	21.180(3)	11.5163(13)	18.064(2)
c (Å)	17.8681(17)	16.898(2)	18.057(2)	31.236(3)
α (°)	90.00	90.00	74.703(3)	89.055(2)
β (°)	91.462(2)	96.082(2)	85.344(3)	77.990(2)
γ (°)	90.00	90.00	67.838(3)	76.191(2)
V (Å^3)	1635.4(3)	3356.2(8)	1934.5(4)	7507.8(14)
Z	4	4	2	2
D_{calc} (Mg/m^3)	1.342	1.098	1.476	1.203
μ (Mo Kα) (mm^{-1})	0.087	0.067	1.044	0.597
F(000)	696	1208	880	2888
θ Range (°)	1.20–29.34	1.55–24.65	1.17–23.74	0.67–22.97
Reflections collected	16956	30884	20276	60807
Reflections unique	4191	5654	5863	20790
R_{int}	0.0297	0.0434	0.0418	0.0575
Data ($I > 2\sigma(I)$)	3149	4282	4294	14205
Parameters refined	229	384	496	1646
Goodness-of-fit (GOF) on F^2	0.688	1.134	1.192	0.932
R_1 [$I > 2\sigma(I)$]	0.0439	0.0578	0.0594	0.0645
wR_2	0.1188	0.1695	0.1727	0.1668