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Benzazolate complexes of pentacoordinate nickel(II). Synthesis, spectroscopic study and luminescent response towards metal cations

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ABSTRACT

$[Ni(mcN_3)(hpbY)](PF_6)$ (**1a**–**3b**) [$mcN_3 = Me_3$–mcN_3 (2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene); Me_4–mcN_3 (its 9-methyl derivative); hpbY = hpbm (2-(2′-hydroxyphenyl) benzimidazolate); hpbx (2-(2′-hydroxyphenyl) benzoxazolate); hpbt, 2-(2′-hydroxy phenyl)benzothiazolate] were synthesized *via* acid–base method and structurally characterized. The complexes exhibit moderate fluorescence intensities. Hetero-atoms of benzazole ligands present in the Ni(II) complexes influence their luminescent properties. These complexes are used for the recognition of different cations of biological and environmental interest. The study of luminescence properties of these complexes reveals that they display good sensitivity towards transition metal ions Zn^{II}, Cu^{II} and Hg^{II}. The complexes act as sensitive fluorescent ON–OFF probe for Cu^{II}. Other metal ions such as Hg^{II} and Zn^{II} gave an enhanced fluorescence response.

1. Introduction

The design and synthesis of fluorescent sensors for the recognition of cations with biological and environmental interest are becoming one of the most challenging realms, not only from the viewpoint of chemistry but also from their potential applications [1]. Thus, zinc is the second most abundant transition metal in many biological systems behind iron, and it plays diverse roles such as regulation of enzymes, DNA binding or recognition, structural cofactors, neural signal transmission, and others [2]. However, many important processes of zinc are still poorly understood [3] in addition, the sensing of zinc is spectroscopically or magnetically silent because of its electronic configuration [4]. Therefore, the detection of zinc is an interesting field of research. Furthermore, it is still a challenge to develop chemosensors that can discriminate zinc from cadmium [5], because both of them are in the same group and have similar properties, which usually cause similar spectral changes after interacting with chemosensors. Copper is not only a significant metallic pollutant but also an essential element for living organisms [6]. Deficiency of copper or zinc can lead to growth or metabolism disorders [7]. Mercury is one of the heavy metals more contaminant with chemical and physical complex properties [8]. It is well-known that their ions tend to bioaccumulate in organisms causing dangerous intoxications [9–11]. Due to their toxic effects and importance to organisms, it is important to develop new chemosensors to able to monitor the presence of copper [12], zinc [13], cadmium [14] and mercury [15], quantitatively.

The use of metal complexes in the design of luminescent responsive probes has been developed over the last years, since they potentially offer improved photophysical attributes over organic fluorophores purely [16]. There have been a number of excellent reviews on transition metal complexes as ion and molecule sensors including several review articles on the metallo-supramolecular chemistry that describe their use in chemical sensing [16a,c]. The binding action of these complexes can be monitored by the changes in the optical properties of the systems. On the other hand, it has been shown in previous reports [17,18] that the benzimidazole-based derivatives are a novel class of N,O-donor ligands that could form sublimable luminescent complexes as possible electroluminescent (EL) materials. Similarly, luminescent properties of related ligands, containing different heteroatoms (NH, O, and S) in the aromatic rings can be expected [18b]. In this paper, we report the syntheses, crystal structures, and luminescent properties of pentacoordinate Ni(II) complexes of aromatic N,O-chelate ligands, namely benzazoles, in general, [Hhpbm, 2-(2′-hydroxyphenyl)benzimidazole, Hhpbx, 2-(2′-hydroxyphenyl)

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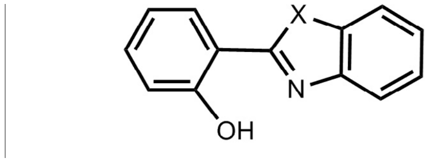

X	benzazole	HhpbY
NH	2-(2'-hydroxylphenyl)benzimidazole	Hhpbm
O	2-(2'-hydroxylphenyl)benzoxazole	Hhpbx
S	2-(2'-hydroxylphenyl)benzothiazole	Hhpbt

Chart 1. Ligands used in this work.

benzoxazole, and Hhpbt, 2-(2′-hydroxyphenyl)benzothiazole] (Chart 1). Extensive spectroscopic characterization and study of photophysical properties is also presented. The electronic transitions in the photoluminescent process, as well as the spectral variations along with the effect of complexation and effect of different heteroatoms were studied. The aim was to synthesize functional luminescent complexes, which display variable response in presence of a given cation of physiological and toxicological importance such as Zn^{II}, Cd^{II}, Hg^{II} or Cu^{II}. The versatility and synthetic accessibility of these complexes makes especially attractive these cation receptors.

2. Experimental

All chemicals were of reagent grade and were used without further purification. Solvents were dried and distilled by general methods before use. The complexes $[Ni(mcN_3)(\mu\text{-}OH)]_2(PF_6)_2$ (mcN_3 = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (Me_3–mcN_3) and its 9-methyl derivative (Me_4–mcN_3)) were prepared by the previously described procedure [19].

2.1. Physical techniques

C, H, N and S analyses were carried out with a microanalyzer Carlo Erba model EA 1108. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. Conductance measurements were performed with a Crison 525 conductimeter (in acetone solution, $c \approx 10^{-3}$ M). ESI-MS analyses were performed on an *Agilent VL mass spectrometer.* The ionization mechanism used was electrospray in positive and negative ion full scan mode using acetonitrile as solvent and nitrogen gas for desolvation. The NMR spectra of $(CD_3)_2CO$ or CD_3CN solutions were recorded on a Bruker spectrometer (AC 200E or AC 300E). $\{^1H–^1H\}$ COSY spectra were recorded on the Bruker 200 MHz spectrometer at 20 °C in CD_3CN solutions with 512 data points in the F1 dimension and 1024 data points in the F2 dimension with a delay time of 500 ms. An unshifted sine-bell-squared weighting function was applied prior to Fourier transformation followed by baseline correction in both dimensions and symmetrization. The UV–Vis spectra (in acetonitrile) were recorded on a UNICAM UV 500 spectrophotometer for 230–800 nm range. DRUV spectra were recorded with a Unicam UV-4 spectrophotometer equipped with a Spectralon RSA-UC-40 Labspere integrating sphere. The solid samples were mixed with dried silica gel to form an homogeneous powder. The mixtures were placed in a home-made cell equipped wtih a quartz window. The intensities were recorded in Kubelka–Munk units: $\log[R/(1-R)^2]$, were R = reflectance. Excitation and emission spectra were recorded on a Jobin Yvon Fluorolog 3-22 spectrofluorometer with a 450 W xenon lamp double-grating monochromators and a TBX-04 photomultiplier. The solution measurements were carried out in a right angle configuration using degassed acetonitrile solutions of the samples in 10 mm quartz fluorescence.

2.2. X-ray data collection and structure determination

Diffraction data were collected in Bruker Smart Apex diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The diffraction frames were integrated using the SAINT package [20] and corrected for absorption with SADABS [21]. Crystallographic data are shown in Table S1. The structures were solved by direct methods and refined anisotropically on F^2 [22]. Hydrogen atoms were introduced in calculated positions.

2.3. Syntheses

In separate experiments, the corresponding benzazole (0.232 mmol) was added to a solution of $[Ni(Me_3–mcN_3)(\mu\text{-}OH)]_2(PF_6)_2$ (100 mg, 0.116 mmol) in acetone (20 mL). The reaction mixture was stirred at room temperature for 2 h. The solution was concentrated to approximately 5 mL and Et_2O (25 mL) was added. The resulting precipitate was filtered and the green solid was washed with several aliquots of diethyl ether and vacuum-dried to give the expected complexes **1a–3a**. The powder isolated in each case was air stable.

The experimental procedure was similar to that described above using $[Ni(Me_4–mcN_3)(\mu\text{-}OH)]_2(PF_6)_2$ (100 mg, 0.112 mmol) and the corresponding benzazole (0.224 mmol) in acetone (20 mL) to prepare complexes **1b–3b**. The green powder isolated in each case was air stable.

*$[Ni(Me_3–mcN_3)(hpbm)](PF_6)$ (**1a**):* Green solid, Yield: 120.7 mg, 83%; elemental *Anal.* Calc. for $C_{25}F_6H_{36}N_5NiO_2P$: C, 46.7; H, 5.6; N, 10.9. Found: C, 46.5; H, 5.5; N, 10.9%. Λ_M: 115.8 S cm^2 mol^{-1}. MS-ESI: *m/z* (%): 478.2 (100) [M]$^+$. IR (Nujol): ν = 3379, 3262, 3168, 1652, 1603, 1549, 841, 558 cm^{-1}.

*$[Ni(Me_3–mcN_3)(hpbx)](PF_6)$ (**2a**):* Green solid, Yield: 112.6 mg, 77%; elemental *Anal.* Calc. for $C_{28}F_6H_{39}N_4NiO_3P$: C, 49.2; H, 5.7; N, 8.2. Found: C, 49.1; H, 5.6; N 8.5%. Λ_M: 117.9 S cm^2 mol^{-1}. MS-ESI: *m/z* (%): 479.2 (100) [M]$^+$. IR (Nujol): ν = 3274, 3255, 1654, 1614, 1552, 836, 558 cm^{-1}.

*$[Ni(Me_3–mcN_3)(hpbt)](PF_6)$ (**3a**):* Green solid, Yield: 129.9 mg, 87%; elemental *Anal.* Calc. for $C_{25}F_6H_{33}N_4NiOPS$: C, 46.8; H, 5.2; N, 8.7; S, 5.0. Found: C, 46.5; H, 5.5; N, 8.5; S, 4.8%. Λ_M: 134.6 S cm^2 mol^{-1}. MS-ESI: *m/z* (%): 495.1 (100) [M]$^+$. IR (Nujol): ν = 3260, 3246, 1655, 1600, 1540, 840, 558 cm^{-1}.

*$[Ni(Me_4–mcN_3)(hpbm)](PF_6)$ (**1b**):* Green solid, Yield: 110.6 mg, 77%; elemental *Anal.* Calc. for $C_{26}F_6H_{36}N_5NiOP$: C, 48.9; H, 5.7; N, 10.9. Found: C, 49.2; H, 5.7; N, 10.5%. Λ_M: 120.6 S cm^2 mol^{-1}. MS-ESI: *m/z* (%): 492.2 (100) [M]$^+$. IR (Nujol): ν = 3371, 3295, 1628, 1603, 1549, 837, 558 cm^{-1}.

*$[Ni(Me_4–mcN_3)(hpbx)](PF_6)$ (**2b**):* Green solid, Yield: 133.6 mg, 93%; elemental *Anal.* Calc. for $C_{26}F_6H_{35}N_4NiO_2P$: C, 48.9; H, 5.5; N, 8.8. Found: C, 48.9; H, 5.4; N, 8.9%. Λ_M: 131.1 S cm^2 mol^{-1}. MS-ESI: *m/z* (%): 493.0 (100) [M]$^+$. IR (Nujol): ν = 3292, 1629, 1615, 1554, 840, 557 cm^{-1}.

*$[Ni(Me_4–mcN_3)(hpbt)](PF_6)$ (**3b**):* Green solid, Yield: 123.9 mg, 84%; elemental *Anal.* Calc. for $C_{26}F_6H_{35}N_4NiOPS$: C, 47.7; H, 5.4; N, 8.5; S, 4.9. Found: C, 47.3; H, 5.5; N, 8.6; S, 4.8%. Λ_M: 128.6 S cm^2 mol^{-1}. MS-ESI: *m/z* (%): 509.1 (100) [M]$^+$. IR (Nujol): ν = 3249, 1646, 1599, 1541, 841, 558 cm^{-1}.

3. Results and discussion

3.1. Synthesis and crystal structures

The complexes under investigation $[Ni(mcN_3)(hpbY)](PF_6)$ (**1a**–**3b**) were synthesized by acid–basic reaction between $[Ni(mcN_3)(\mu\text{-}OH)]_2(PF_6)_2$ [19] and the corresponding benzazole (Chart 1) in acetone at room temperature, as depicted in Scheme 1.