



Self-assembly of a tridentate Schiff-base ligand with Zn(II) in the presence of lanthanides: Novel crystal structures and spectroscopic properties

Monika Wałęsa-Chorab, Adam Gorczyński, Maciej Kubicki, Zbigniew Hnatejko, Violetta Patroniak*

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60780 Poznań, Poland

ARTICLE INFO

Article history:

Received 18 July 2011

Accepted 10 August 2011

Available online 7 September 2011

Keywords:

Schiff-base ligand

Self-assembly

Zinc

Lanthanides

Luminescence

ABSTRACT

Condensation of picolinaldehyde with methyl 4-amino-3-hydroxy-benzoate resulted in the acquisition of a tridentate Schiff-base ligand (HL) which contains a structural moiety typical of octahedrally cored grid-type analogs. Reactions of HL with $Zn(NO_3)_2$ in the presence of $Ln(NO_3)_3$ [$Ln = Sm(III), Tb(III)$ and $Yb(III)$] result in two types of complexes, viz. $[Zn(HL)(L)]_2[Ln(NO_3)_5]$ [$Sm(III)$, **1a** and $Tb(III)$, **1b**] and $[Zn(HL)L]_2[Yb(NO_3)_5] \cdot C_3H_6O$ (**1c**). Despite applying two different synthetic protocols, the transition metal ion displayed a greater propensity towards the meridional tridentate pocket, which is reflected by XRD analysis, the ESI-MS technique and further supported by elemental analysis and IR characterization of each compound. In addition, we have compared the luminescence properties of **1a**, **1b** and **1c** with the previously synthesized $[Zn(HL)(L)]_2[Zn(NO_3)_4]$ (**1d**) to investigate whether a different metal in the outer coordination sphere could somehow tune the compounds' spectral behavior.

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1. Introduction

Since the pioneering works of Pedersen, Lehn and Cram, which became the underpinnings for modern supramolecular chemistry, the so called 'chemistry beyond the molecule' [1,2] has become a substantial scientific domain marking itself as an interdisciplinary field of research. Its uniqueness lies in utilizing specific, non-covalent interactions, thus comprising the intrinsic properties of the molecules to organize and form a variety of sophisticated, self-assembled architectures ranging from host–guest receptors [3–6] and nanomolecular devices [7–12] to supramolecular coordination polymers [13–16]. Dative and H-bondings play a crucial role in the phenomena mentioned, not only due to their relative higher stability in comparison with van der Waals and π – π interactions – although their role must not be neglected [17,18], but also thanks to their directionality and reversibility. Nevertheless it is nature itself where the self-assembly process may bewilder with its beauty from DNA onwards [19], and from where the inspiration may be derived in the synthetic systems construction, e.g. the assembly of polyalanine or poly(glycinealanine) repeat sequences in spider silk which contribute to its unrivaled mechanical tensile strength [20], or the binding between avidin and biotin resulting in blood clotting [21].

What has become one of the biggest challenges, that would fully utilize the true potential of supramolecular chemistry, is *a priori* evaluation of molecular systems that would lead to pre-

programmed, perfectly controlled self-assembly [22]. Such a prediction is particularly difficult in coordinative systems which are to be employed with dissimilar metal centers, an emphasis being put on lanthanides due to their high coordination numbers and stereochemical non-rigidity. Schiff-base ligands, whose biological resemblance and facile, straightforward synthetic pathways with the possibility of applying a metal-mediated *in situ* protocol, have made a contribution of lasting value to the development of coordination chemistry. The nature, quantity and relative position of donor atoms make the controlled construction of supramolecular structures to a certain extent possible even in the presence of lanthanides, and the importance of phenoxy groups must be stressed as their presence may induce the formation of phenoxo bridges, which is often encountered [23,24]. The possibility of constructing mixed *d* and *f* supramolecular systems appears to be exceptionally appealing, since they may form single molecule magnets (SMMs) [25–27] or metal-organic frameworks (MOFs) [28–33].

Our earlier works concerning tridentate NNO Schiff-base ligands resulted in the one pot synthesis of homo- and heterodinuclear complexes of zinc(II) and lanthanide(III) ions [34], which was followed by the acquisition of novel Schiff-base coordinative species and their further structural and spectroscopic research in terms of solely the coordination of the transition metal ions [35]. Out of three previously investigated ligands, methyl 3-hydroxy-4-(pyridin-2-ylmethyleneamino)benzoate (HL) (Fig. 1) and its complexes were found to crystallize in a relatively facile manner in comparison with the others, hence it was chosen for further studies.

* Corresponding author. Fax: +48 618291508.

E-mail address: violapat@amu.edu.pl (V. Patroniak).

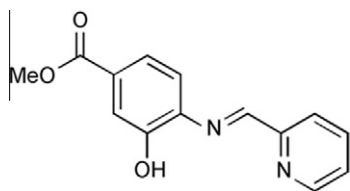


Fig. 1. Chemical structure of methyl 4-hydroxy-3-(pyridin-2-ylmethyleneamino)benzoate HL ($C_{14}H_{12}N_2O_3$).

With particular regard to the latter studies of transition metal grid corner analogs, we focused herein on the aspect of lanthanide ion incorporation – their propensity to occupy a tridentate donor pocket in the presence of zinc(II) ions, as well as how they would tune the luminescent properties of the compounds obtained.

2. Experimental

2.1. General

The metal salts were used without further purification as supplied from Aldrich. The ligand HL ($C_{14}H_{12}N_2O_3$) was prepared in a similar manner, as published in our earlier research [35]. Mass spectra for acetonitrile solutions ($\sim 10^{-4}$ M) were determined using a Waters Micromass ZQ spectrometer. Sample solutions were introduced into the mass spectrometer source with a syringe pump at a flow rate of $40 \mu\text{L min}^{-1}$ with a capillary voltage of +3 kV and a desolvation temperature of 300°C . The source temperature was 120°C . The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from $m/z = 100$ – 2000 for 6 s, and 10 scans were summed to obtain the final spectrum. Microanalyses were obtained using a Perkin–Elmer 2400 CHN microanalyzer. IR spectra were obtained with a Perkin–Elmer 580 spectrophotometer and are reported in cm^{-1} . All absorption spectra were recorded with a Shimadzu UVPC 2001 spectrophotometer, between 200 and 800 nm, in 10×10 mm quartz cells using 5×10^{-5} M solutions with respect to the metal ion. Excitation and emission spectra were measured at room temperature on a Perkin–Elmer MPF3 spectrofluorimeter with an excitation slit at 10 nm and an emission slit at 2.5 nm.

2.2. Complex preparation: general procedures

The complexes were synthesized according to both of the following procedures, maintaining a fixed molar ratio of 1:1:3 respectively for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and HL:

- (1) 15.0 mg (58.5 μmol) HL was dissolved in 10 ml of MeCN and 19.5 μmol of lanthanide nitrate was added, which was concomitant with a change in color. After 10–20 min, depending on the lanthanide chosen, a yellowish precipitate formed. Subsequent 24 h of stirring ended with the addition of 5.8 mg (19.5 μmol) of zinc nitrate, prior to which 5 ml of MeOH was injected via syringe to dissolve the solid formed. Successive 24 h of stirring was followed by solvent evaporation under reduced pressure, then gradual addition of consecutively a MeOH/MeCN (1:1 v/v) mixture and Et_2O yielded the complexes as orange solids.
- (2) The distinctive feature of the second procedure was the simultaneous addition of both the transition metal and lanthanide nitrates (one pot reaction), which resulted in 48 h stirring and a lack of MeOH solvent in the initial phase of the synthesis.

2.2.1. $[\text{Zn}(\text{HL})(\text{L})]_2[\text{Sm}(\text{NO}_3)_5]$ (**1a**)

ESI-MS(+) m/z : 575 (5) $[\text{Zn}(\text{HL})(\text{L})]^+$, 319 (100) $[\text{Zn}(\text{L})]^+$, 257 (20) $[\text{H}_2\text{L}]^+$. ESI-MS(–) m/z : 400 (100) $[\text{Sm}(\text{NO}_3)_4]^-$. IR (KBr, cm^{-1}): $\nu_s(\text{O-H})$ 3383, $\nu(\text{C-H})_{\text{ar}}$ 3063, 3026, $\nu_{\text{as}}(\text{CH}_3)$ 2958, $\nu_s(\text{CH}_3)$ 2850, $\nu_s(\text{C=O})$ 1715, $\nu(\text{C=C})_{\text{py}}$ 1613, 1594, 1569, $\nu_{\text{as}}(\text{NO}_2)$ 1470, $\nu(\text{C=N})_{\text{py}}$ 1456, $\nu_{\text{as}}(\text{NO}_3^-)$ 1384, $\nu_s(\text{NO}_2)$ 1312, $\nu_s(\text{C-O})$ 1228, $\rho(\text{C-H})_{\text{py}}$ 1123, 1070, $\delta(\text{OH})$ 894, $\gamma(\text{C-H})_{\text{py}}$ 777, 766, 746, 634, 514. Anal. Calc. for $[\text{Zn}(\text{HL})(\text{L})]_2[\text{Sm}(\text{NO}_3)_5]$ (1614.20): C, 41.67; H, 2.97; N, 11.28. Found: C, 41.60; H, 3.03; N, 11.25%.

2.2.2. $[\text{Zn}(\text{HL})(\text{L})]_2[\text{Tb}(\text{NO}_3)_5]$ (**1b**)

ESI-MS(+) m/z : 575 (5) $[\text{Zn}(\text{HL})(\text{L})]^+$, 319 (70) $[\text{Zn}(\text{L})]^+$, 257 (100) $[\text{H}_2\text{L}]^+$. ESI-MS(–) m/z : 407 (100) $[\text{Tb}(\text{NO}_3)_4]^-$. IR (KBr, cm^{-1}): $\nu_s(\text{O-H})$ 3382, $\nu(\text{C-H})_{\text{ar}}$ 3062, 3026, $\nu_{\text{as}}(\text{CH}_3)$ 2958, $\nu_s(\text{CH}_3)$ 2850, $\nu_s(\text{C=O})$ 1716, $\nu(\text{C=C})_{\text{py}}$ 1612, 1594, 1568, $\nu_{\text{as}}(\text{NO}_2)$ 1472, $\nu(\text{C=N})_{\text{py}}$ 1455, $\nu_{\text{as}}(\text{NO}_3^-)$ 1384, $\nu_s(\text{NO}_2)$ 1313, $\nu_s(\text{C-O})$ 1229, $\rho(\text{C-H})_{\text{py}}$ 1123, 1070, $\delta(\text{OH})$ 895, $\gamma(\text{C-H})_{\text{py}}$ 777, 766, 746, 634, 514. Anal. Calc. for $[\text{Zn}(\text{HL})(\text{L})]_2[\text{Tb}(\text{NO}_3)_5]$ (1622.72): C, 41.45; H, 2.86; N, 11.22. Found: C, 41.54; H, 2.85; N, 11.27%.

2.2.3. $[\text{Zn}(\text{HL})(\text{L})]_2[\text{Yb}(\text{NO}_3)_5] \cdot \text{C}_3\text{H}_6\text{O}$ (**1c**)

ESI-MS(+) m/z : 319 (100) $[\text{Zn}(\text{L})]^+$. ESI-MS(–) m/z : 422 (100) $[\text{Yb}(\text{NO}_3)_4]^-$. IR (KBr, cm^{-1}): $\nu_s(\text{O-H})$ 3371, $\nu(\text{C-H})_{\text{ar}}$ 3060, 3023, $\nu_{\text{as}}(\text{CH}_3)$ 2951, $\nu_s(\text{CH}_3)$ 2855, $\nu_s(\text{C=O})$ 1712, $\nu(\text{C=C})_{\text{py}}$ 1612, 1594, 1567, $\nu_{\text{as}}(\text{NO}_2)$ 1475, $\nu(\text{C=N})_{\text{py}}$ 1457, $\nu_{\text{as}}(\text{NO}_3^-)$ 1384, $\nu_s(\text{NO}_2)$ 1313, $\nu_s(\text{C-O})$ 1228, $\rho(\text{C-H})_{\text{py}}$ 1122, 1070, $\delta(\text{OH})$ 890, $\gamma(\text{C-H})_{\text{py}}$ 777, 746, 634, 514. Anal. Calc. for $[\text{Zn}(\text{HL})(\text{L})]_2[\text{Yb}(\text{NO}_3)_5] \cdot \text{C}_3\text{H}_6\text{O}$ (1696.93): C, 41.76; H, 3.21; N, 10.73. Found: C, 41.74; H, 3.20; N, 10.73%.

2.3. X-ray structure determination of complexes **1a–c**

Acquisition of crystals suitable for XRD analysis was performed by means of slow diffusion of diethyl ether (**1a** and **1b**) or isopropanol (**1c**) into concentrated methanol solutions of the purified complexes. Diffraction data were collected at room temperature by the ω -scan technique, for **1a** and **1c** on an Xcalibur diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), and for **1b** on a SuperNova diffractometer with mirror-monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The data were corrected for Lorentz-polarization and absorption effects [36]. Accurate unit-cell parameters were determined by a least-squares fit of 6253 (**1a**), 6903 (**1b**) and 16079 (**1c**) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SIR92 [37] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [38]. Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in calculated positions, and refined as a 'riding model' with the isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times the U_{eq} value for the appropriate non-hydrogen atom. Hydrogen atoms involved in O–H...O hydrogen bonds were found in the difference Fourier maps in **1c** (and then refined), but in **1a** and **1b** they were put in the special positions in the midpoints of the O...O contacts. The U_{iso} for these atoms were refined and their reasonable refinement might be regarded as additional proof for the significance of such an assignment. Relevant crystal data are listed in Table 1, together with refinement details. In **1a** and **1b**, the nitro groups are partially resolved and were refined with two alternative positions. Weak constraints were applied to the displacement parameters of these groups. In **1c** the partially occupied solvent, the isopropanol molecule, was found occupying the voids in the crystal structure.

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