Polyhedron 31 (2012) 136–142

Contents lists available at SciVerse ScienceDirect

Polyhedron

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

# Syntheses, structures and photoelectronic properties of a series of tri- and tetra-nuclear metal complexes based on a 36-membered tetraphenol macrocyclic ligand

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ARTICLE INFO

*Article history:*
Received 27 June 2011
Accepted 6 September 2011
Available online 16 September 2011

*Keywords:*
Zinc
Macrocyclic ligand
Surface photovoltage spectroscopy

ABSTRACT

In this article, tetranuclear $Zn^{II}$ coordination complexes $[Zn_4L(\mu_2\text{-}OH)_2]\cdot 2(NO_3)\cdot 6(CH_3OH)\cdot H_2O$ (**1**) and $[Zn_4L(\mu_2\text{-}OH)_2(H_2O)_2]\cdot(p\text{-bdc})\cdot 2(CH_3OH)\cdot 3H_2O$ (**2**), dinuclear $Zn^{II}$ complex $[Zn_4L(NH_2\text{-bdc})_2]\cdot 2(CH_3OH)\cdot 3H_2O$ (**3**), and trinuclear $Cd^{II}$ complexes $[Cd_3L(m\text{-bdc})]\cdot 6.5H_2O$ (**4**) and $[Cd_3L(NH_2\text{-bdc})]\cdot 5.5H_2O$ (**5**), based on a tetraphenol 36-membered macrocycle (L) having four ethylenediamine and four 2,6-diformyl-4-methylphenol functionalities, have been synthesized at room temperature (*p*-bdc = 1,4-benzenedicarboxylate, $NH_2$-bdc = 5-aminoisophthalate and *m*-bdc = 1,3-benzenedicarboxylate). In **1** and **2**, four $Zn^{II}$ centers are bridged by phenoxide and hydroxy atoms of the L ligands to form tetranuclear $Zn^{II}$ complexes. The inorganic and organic anions in **1** and **2** do not coordinate to $Zn^{II}$ centers, but act as counter anions. In **3**, two $Zn^{II}$ centers are bridged by two phenoxide O atoms to form a $Zn^{II}$ cluster ($Zn_2O_2N_4$). Moreover, two ($Zn_2O_2N_4$) clusters within the ring of the L ligand are further bridged by two $NH_2$-bdc anions in a monodentate fashion. Compound **4** possesses the trinuclear $Cd^{II}$ clusters ($Cd_3N_8O_8$), which has a similar structure to compound **5**. The trinuclear $Cd^{II}$ clusters are bridged by the dicarboxylate anions to yield an infinite coordination polymers chain. The photoelectric transfer properties of complexes **1**, **2** and **4** were investigated by surface photovoltage spectroscopy (SPS) and the field-induced surface photovoltage spectra (FISPS) techniques. The results reveal that the complexes exhibit positive surface photovoltage (SPV) responses in the range of 300–600 nm, possessing the *p*-type semiconductor characteristics. So far, the surface photovoltage properties of the macrocycle complexes based on tetraphenol macrocyclic ligands were investigated for the first time. Moreover, elemental analyses, IR spectra, and luminescent properties of these compounds were also studied.



## 1. Introduction

In recent years, the research for macrocyclic complexes is of intense interest, not only because of their intriguing variety of architectures and multinuclear metals but also because of their fascinating extraordinary properties in the study of catalysis, metalloenzyme and molecular recognition [1]. Currently, there have been extensive studies on the synthesis and construction of the phenol-based metal complexes derived from 2,6-diformyl-4-methylphenol or its analogs with amines [2]. In this regard, Ōkawa and co-workers have reviewed the progress of heterodinuclear metal complexes based on phenol-base compartmental macrocycles as well as their analogs having auxiliaries at amino nitrogens [3a]. At the same time, phenol-based macrocylic polyamine dinucleating ligand having two metal-binding sites have been widely developed in the construction of dinuclear metal complexes [3]. Several studies on the complexes of tetraphenol macrocyclic ligands have been reported, and these multinuclear complexes display interesting magnetic, electronic, and/or catalytic properties [4].

So far, the property studies of macrocyclic complexes are mainly focused on electrochemical properties, intermolecular electron-transfer, electronic structure of mixed-valence states, magneto-structural correlation, or selective substrate binding of bimetallic systems [5]. Nonetheless, the photoelectronic properties of the complexes based on tetraphenol macrocyclic ligand have not been investigated with the surface photovoltage (SPV) method.

The SPS technique, with a very high sensitivity, can be used to investigate the photophysics of the excited states and the surface charge behavior of the sample, which are widely used to

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doi:10.1016/j.poly.2011.09.005

study the photoelectric properties of phthalocyanine and porphyrin coordination complexes [6]. In addition, field-induced surface photovoltage spectroscopy (FISPS) technique can demonstrate the photoelectric properties of semiconductors [7]. So far, only few studies on the photoelectric properties of coordination complexes have been investigated [8].

In this article, a series of $Zn^{II}$ and $Cd^{II}$ complexes based on the 36-membered tetraphenol macrocyclic ligand (L), namely $[Zn_4L(\mu_2\text{-}OH)_2]\cdot 2(NO_3)\cdot 6(CH_3OH)\cdot H_2O$ (**1**), $[Zn_4L(\mu_2\text{-}OH)_2(H_2O)_2]\cdot$(*p*-bdc)$\cdot 2(CH_3OH)\cdot 3H_2O$ (**2**), $[Zn_4L(NH_2\text{-}bdc)_2]\cdot 2(CH_3OH)\cdot 3H_2O$ (**3**), $[Cd_3L(m\text{-}bdc)]\cdot 6.5H_2O$ (**4**), and $[Cd_3L(NH_2\text{-}bdc)]\cdot 5.5H_2O$ (**5**), have been synthesized through variations of the structurally-different anions (*m*-bdc = 1,3-benzenedicarboxylate, *p*-bdc = 1,4-benzenedicarboxylate, $NH_2$-bdc = 5-aminoisophthalate). The surface photovoltage spectroscopy (SPS) and field-induced surface photovolt age spectroscopy (FISPS) properties have been investigated. In addition, the photoluminescent properties of these tetraphenol macrocyclic phenol-based polymers have also been studied.

## 2. Experimental

### 2.1. Materials and methods

The tetraphenol macrocyclic ligand L was synthesized in accordance with the previous report [4e]. Typically, the 2,6-diformyl-4-methylphenol (18.8 g, 0.1 mol), 1,2-diaminoethane (2.4 g, 0.4 mol), $Mg(OAc)_2\cdot 4H_2O$ (42.8 g, 0.2 mol), and $Mg(NO_3)_2\cdot 6H_2O$ (36.8 g, 0.2 mol) were mixed in methanol at 50 °C over a period of 6 h. An orange yellow magnesium complex that deposited was collected and reduced with $NaBH_4$ in methanol. Acidification of the solution with HCl (8 M) followed by cooling afforded the colorless crystals of $H_4L\cdot 8HC1$, an aqueous solution of which on treatment with concentrated ammonia solution followed by extraction with $CH_2Cl_2$ and recrystallization from $CHCl_3$–$CH_3OH$ gave $H_4L$ (yield: 35%). Other reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer, and the FT-IR spectra were recorded from KBr pellets in range 4000–400 $cm^{-1}$ on a Mattson Alpha-Centauri spectrometer. The solid-state emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer at room temperature. The surface photovoltage spectroscopic (SPS) data and the field-induced surface photovoltage spectroscopic (FISPS) data were measured with a solid junction photovoltaic cell ITO/sample/ITO by a light source-monochromator-lock-in detection technique [9]. ITO glass was used as the transparent front and back electrodes. FISPS were obtained with a dc bias applied to the two sides of the sample cell. The measurement was performed under atmospheric pressure and ambient temperature (about 20 ± 2 °C).

### 2.2. Syntheses

#### 2.2.1. Synthesis of $[Zn_4L(\mu_2\text{-}OH)_2]\cdot 2(NO_3)\cdot 6(CH_3OH)\cdot H_2O$ (1)

An aqueous solution (5 mL) of $Zn(NO_3)_2\cdot 6H_2O$ (0.12 g, 0.4 mmol) was added to methanol solution (15 mL) of L (0.077 g, 0.1 mmol) and stirred for 30 min, then filtered. Colorless crystals of **1** were obtained by evaporation of the solution for a week at room temperature (yield: 65%). *Anal.* Calc. for $C_{50}H_{86}N_{10}O_{19}Zn_4$: C, 43.11; H, 6.22; N, 10.06. Found: C, 43.08; H, 6.26; N, 10.10%. IR ($cm^{-1}$): 3296 (ms), 3027 (ms), 2918 (ms), 2852 (w), 1748 (w), 1605 (s), 1484 (vs), 1453 (vs), 1402 (vs), 1303 (s), 1378 (ms), 1219 (ms), 1162 (w), 1106 (w), 1038 (ms), 1012 (w), 876 (ms), 821 (ms), 780 (w), 747 (w), 719 (w).

#### 2.2.2. Syntheses of $[Zn_4L(\mu_2\text{-}OH)_2(H_2O)_2]\cdot$(p-bdc)$\cdot 2(CH_3OH)\cdot 3H_2O$ (2) and $[Zn_4L(NH_2\text{-}bdc)_2]\cdot 2(CH_3OH)\cdot 3H_2O$ (3)

An aqueous solution (5 mL) of $Zn(Ac)_2\cdot 2H_2O$ (0.088 g, 0.4 mmol) was added to methanol solution (15 mL) of L (0.077 g, 0.1 mmol) and stirred for 30 min, then filtered. Afterward, the 1,4-benzenedicarboxylic acid (0.068 g, 0.4 mmol) was added to the filtrate and stirred for several minutes, and a white precipitate formed. The precipitate was dissolved by dropwise addition of an aqueous solution of $NH_3$ (14 M). The solution was kept for one week at room temperature to produced single crystals suitable for X-ray analyses (yield: 71%). A procedure is similar to that used for compound **3**, with the added 5-aminoisophthalic acid (0.072 g, 0.40 mmol) in **3** (yield: 53%). *Anal.* Calc. for $C_{53}H_{78}N_{10}O_{14}Zn_4$ (compound **2**): C, 47.47; H, 5.86; N, 10.45. Found: C, 47.51; H, 5.83; N, 10.42%. *Anal.* Calc. for $C_{62}H_{80}N_{10}O_{17}Zn_4$ (compound **3**): C, 49.68; H, 5.38; N, 9.34. Found: C, 49.71; H, 5.35; N, 9.37%. IR ($cm^{-1}$) for compound **2**: 3420 (ms), 3256 (ms), 2915 (ms), 2862 (ms), 1577 (vs), 1471 (vs), 1361 (vs), 1301 (s), 1235 (ms), 1159 (w), 1130 (w), 1090 (w), 1068 (ms), 1037 (ms), 1014 (w), 956 (w), 924 (w), 865 (ms), 815 (ms), 790 (s), 750 (ms), 682 (w), 532 (w), 508 (w). IR ($cm^{-1}$) for compound **3**: 3589 (ms), 3239 (s), 2940 (ms), 2873 (ms), 1621 (s), 1562 (vs), 1430 (vs), 1352 (s), 1301 (ms), 1260 (ms), 1237 (s), 1172 (w), 1130 (ms), 1112 (ms), 1094 (w), 1068 (w), 1023 (w), 972 (ms), 916 (ms), 897 (ms), 839 (s), 793 (ms), 776 (s), 722 (ms), 673 (w), 582 (w), 536 (w), 485 (ms).

#### 2.2.3. Syntheses of $[Cd_3L(m\text{-}bdc)]\cdot(CH_3OH)\cdot 6.5H_2O$ (4) and $[Cd_3L(NH_2\text{-}bdc)]\cdot 5.5H_2O$ (5)

The preparation of **4** was similar to that of **2** except that $Cd(Ac)_2\cdot 2H_2O$ (0.11 g, 0.4 mmol) and 1,3-benzenedicarboxylic acid (0.068 g, 0.4 mmol) were used instead of $Zn(Ac)_2\cdot 2H_2O$ and 1,4-benzenedicarboxylic acid (yield: 47%). The preparation of **5** was similar to that of 3 except that $Cd(Ac)_2\cdot 2H_2O$ (0.11 g, 0.4 mmol) was used instead of $Zn(Ac)_2\cdot 2H_2O$ (yield: 53%). *Anal.* Calc. for $C_{106}H_{158}N_{16}O_{29}Cd_6$ (compound **4**): C, 45.55; H, 5.67; N, 8.02. Found: C, 45.59; H, 5.59; N, 7.95%. *Anal.* Calc. for $C_{104}H_{138}N_{18}O_{27}Cd_6$ (compound **5**): C, 45.48; H, 5.06; N, 9.18. Found: C, 45.51; H, 5.13; N, 9.15%. IR ($cm^{-1}$) for compound **4**: 3422 (ms), 3260 (ms), 2909 (ms), 2856 (ms), 1605 (vs), 1545 (vs), 1468 (vs), 1371 (s), 1303 (s), 1259 (ms), 1189 (w), 1159 (w), 1072 (w), 1004 (w), 974 (w), 911 (w), 861 (ms), 784 (ms), 718 (ms), 555 (w), 482 (ms). IR ($cm^{-1}$) for compound **5**: 3420 (ms), 3258 (ms), 2907 (ms), 2855 (ms), 1610 (s), 1555 (vs), 1467 (vs), 1364 (s), 1303 (s), 1259 (s), 1189 (w), 1159 (w), 1057 (w), 1001 (w), 897 (w), 863 (ms), 781 (s), 722 (ms), 672 (w), 541 (w), 482 (ms).

### 2.3. X-ray crystallography

Experimental details of the X-ray analyses are provided in Table 1. Diffraction intensities for **1**, **2**, **4** and **5** were collected on a Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) at 293 K. Diffraction data for **3** was collected on a Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Cu Kα radiation ($\lambda$ = 1.54184 Å) at 293 K. The structures were solved with the direct method of SHELXS-97 [10] and refined with full-matrix least-squares techniques using the SHELXL-97 program [11] within WINGX [12]. Non-hydrogen atoms were refined anisotropically except solvent molecules. Non-hydrogen atoms of C25, C26, O8, O9 in **1**, C27 in **2**, O7, O8, C40 in **3** were refined isotropically. The hydrogen atoms attached to carbons were generated geometrically; the aqua hydrogen atoms of O1W and O2W in **2** were located from difference Fourier maps and refined with isotropic displacement parameters; the hydrogen atoms associated with the other water molecules were not located from the difference Fourier maps.