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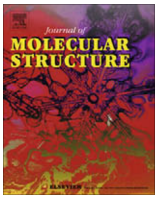

Syntheses, crystal structures, third-order nonlinear optical properties and thermal properties of two infinite (6, 3) net complexes

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ABSTRACT

Two new complexes $\{[Co(bbbm)_{1.5}(NO_3)_2]\cdot H_2O\}_n$ (**1**) and $[Cd(bbbm)_{1.5}(NO_3)_2]_n$ (**2**) (bbbm = 1,1'-(1,4-butanediyl)bis-1H-benzimidazole) have been synthesized and structurally characterized. Both complexes are built up by two-dimensional coordination networks with (6, 3) nets. The third-order nonlinear optical (NLO) properties of the two complexes are determined and the results show that they not only possess large third-order NLO absorptive effects, but also display strong refractive behaviors. The hyperpolarizability $|\gamma|$ values are 2.2×10^{-29} esu for complex **1**, and 1.6×10^{-30} esu for complex **2**. The NLO effective of complex **1** is stronger than that of **2** due to the decreased π back-donation capacity from Co(II) to Cd(II). Thermal analysis studies show that complex **1** is less stable and begins to decompose at 131 °C. While complex **2** is stable up to 257 °C.

1. Introduction

A significant amount of research has been dedicated to the design and construction of complexes due to their special use in catalysis, magnetism, electrical conductivity, optical materials, and so on [1–4]. Among the distinct factors involved in the syntheses of complexes, ligand design is often a useful way of manipulating the overall resulting frameworks. Since the flexible-ligands can easily bend or twist resulting in the diverse coordination modes. So up to now, a lot of flexible-ligand-containing complexes with special structures such as concavo–convex chain complex $[Zn(bbbt)(NCS)_2]_n$ (bbbt = 1,1'-(1,4-butanediyl)bis-1H-benzotriazole) [5], double-chain complexes $[M(NCS)_2(bpa)_2]_n$ (M = Fe, Co, Ni, bpa = 1,2-bis(4-pyridyl)ethane) [6], single-stranded helical chain complexes $[Cu(ipa)(2,2'\text{-}bpy)]_n\cdot 2nH_2O$, $[Cu_2(ipa)_2(phen)_2\text{-}H_2O]_n$ (ipa = isophthalate, phen = 1,10-phenanthroline), $[Cu(oba)(phen)]_n$ (oba = 4,4'-oxybis(benzoate)) [7], 2-D rhombohedral grid complexes $[M(bbbt)_2(NCS)_2]_n$ (M = Co, Mn, Cd, bbbt = 1,1'-(1,4-butanediyl)bis-1H-benzotriazole) [8], and 3-D complex $[Cd_2(SO_4)_2(Py_2C_3H_6)_3(H_2O)_{2.7}]\cdot 4.5H_2O$ [9], *etc.* have been reported. On the other hand, in order to exploit the potential applications of the complexes, researchers have paid much attention on the investigation of their physical and chemical properties. There have been a lot of reports on the magnetic, catalytic, biological, ion exchange properties of the complexes [5,6,10–13]. For example, square grid complex $\{[Cd(bpy)_2](NO_3)_2\}_n$ can accelerate cyanosilylation reaction [10]; honeycomb-like complex Ag-tris(*p*-cyanobenzene)ethynyl-benzene exhibits auxetic properties [11]; 3-D complex $\{[Cd_3(\mu_3\text{-}OH)L_3(py)_6](ClO_4)_2\}_n$ (L = 4-[2-(4-pyridyl)ethenyl]benzoate) has a powder SHG (second harmonic generation) efficiency approximately 10 times higher than that of technologically useful potassium dihydrogen phosphate (KDP) [12]; 3-D porous complex $[Ag(4,4'\text{-}bpy)(NO_3)]_n$ shows ion exchange properties [13]. But less investigation on the third-order NLO properties of complexes was reported. Our group has synthesized some complexes such as $[M(bbbt)_2(NCS)_2]_n$ (M = Co, Mn, Cd, bbbt = 1,1'-(1,4-butanediyl)bis-1H-benzotriazole), $[Mn(N_3)_2(bbp)_2]_n$, $\{[Mn(NCS)_2(bbp)_2]\cdot 0.25H_2O\}_n$ and so on [5,8,14–16], and investigated their third-order NLO properties. In order to enrich the categories and numbers of complexes with good NLO properties, here we synthesized two new complexes with flexible-ligand 1,1'-(1,4-butanediyl)bis-1H-benzimidazole (bbbm) and studied their third-order NLO properties and thermal properties.

2. Experimental

2.1. Materials and general details

Commercially available solvents and chemicals were used without further purification. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Carbon, hydrogen and nitrogen analyses were performed with Flash EA 1112 elemental analyzer. UV–vis

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spectra were recorded, ranging from 275 nm to 1000 nm, on a Hitachi-220A ultraviolet–visible spectrophotometer.

2.2. Preparation of the ligand

Ligand 1,1'-(1,4-butanediyl)bis-1H-benzimidazole(bbbm) was prepared according to the literature with some modification [17]. Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.48; H, 6.25; N, 19.30. Found: C, 74.68; H, 6.38; N, 19.43%. IR (KBr)/cm^{-1}: 3083 m, 2924 m, 1496s, 1462s, 1383s, 1332s, 751s.

2.3. Preparation of complex $\{[Co(bbbm)_{1.5}(NO_3)_2]\cdot H_2O\}_n$ (1)

A methanol solution (8 ml) of bbbm (0.2 mmol) was dropwise added into an aqueous solution (1 ml) of $Co(NO_3)_2\cdot 6H_2O$ (0.1 mmol) to give a clear solution. The resulting solution was allowed to stand in air at room temperature. Crystals suitable for X-ray diffraction were obtained after about two months. Anal. Calcd for $C_{27}H_{29}CoN_8O_7$: C, 50.95; H, 4.59; N, 17.60. Found: C, 51.06; H, 4.72; N, 17.45%. IR (KBr)/cm^{-1}: 3106w, 2929w, 1514s, 1465s, 1385s, 1310s, 753s.

2.4. Preparation of complex $[Cd(bbbm)_{1.5}(NO_3)_2]_n$ (2)

The procedure was the same as that for **1** except that $Co(NO_3)_2\cdot 6H_2O$ was replaced by $Cd(NO_3)_2\cdot 4H_2O$. Anal. Calcd for $C_{27}H_{27}CdN_8O_6$: C, 48.26; H, 4.05; N 16.68. Found: C, 48.01; H, 3.98%; N, 17.02. IR (KBr)/cm^{-1}: 3101w, 2933w, 1505s, 1457s, 1385s, 1304s, 748s.

2.5. Crystal structure determination

A crystal suitable for X-ray determination was mounted on a glass fiber. All data were collected at room temperature on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and expanded using Fourier techniques. All nonhydrogen atoms were refined anisotropically, whereas the isotropic hydrogen atoms were introduced at calculated positions using a riding model (the hydrogen atoms on the water were found on a Fourier difference map and were included in a fixed position). The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using *SHELXL-97* crystallographic software package [18]. Due to the defect of our instrument (Rigaku RAXIS-IV), the number of measured reflections for each structure is significantly below 100% (i.e. 78% for complex **1** and 81% for complex **2**). Table 1 shows crystallographic crystal data and processing parameters for complexes **1** and **2**. Selected bond lengths and bond angles are listed in Table 2.

Crystallographic data reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication. CCD numbers are 183325 and 183327.

2.6. Molecular weight measurements

The molecular weight and molecular weight distribution of the complexes were determined at 40 °C with Gel Permeation Chromatography (Aglient 1100 liquid chromatography, equipped with a refractive index detector, μ-Styragel columns and calibrated with standard polystyrene), using DMF as eluent and a flow rate of 1.0 ml min^{-1}.

Table 1
Crystal data and structure refinement for complexes **1** and **2**.

Complexes	1	2
Empirical formula	$C_{27}H_{29}CoN_8O_7$	$C_{27}H_{27}CdN_8O_6$
Formula weight	636.51	671.97
Temperature [K]	291(2)	291(2)
Radiation	Mo-Kα	Mo-Kα
Wavelength [Å]	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
Crystal dimensions [mm^3]	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20
a [Å]	8.9565(18)	7.7464(15)
b [Å]	10.660(2)	34.874(7)
c [Å]	15.740(3)	10.926(2)
α [°]	82.42(3)	90
β [°]	87.27(3)	105.67(3)
γ [°]	79.88(3)	90
V [$Å^3$]	1466.05(5)	2841.8(10)
Z	2	4
F(0 0 0)	660	1364
ρ [g cm^{-3}]	1.442	1.571
μ [mm^{-1}]	0.644	0.825
Data/restrains/ parameters	4051/0/388	4248/0/404
Goodness-of-fit on F^2	1.054	1.045
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0584$, $wR2 = 0.1570$	$R1 = 0.0413$, $wR2 = 0.0938$
R indices (all data)	$R1 = 0.0678$, $wR2 = 0.1645$	$R1 = 0.0525$, $wR2 = 0.0983$
Largest diff. peak and hole	0.763 and −0.613 e $Å^{-3}$	0.897 and −0.587 e $Å^{-3}$

Table 2
Selected bond lengths [Å] and angles [°] for complexes **1** and **2**.

Complex **1**			
Co(1)–N(5)	2.068(3)	Co(1)–N(3)	2.096(3)
Co(1)–O(2)	2.138(3)	Co(1)–N(1)	2.153(4)
Co(1)–O(1)	2.227(3)	Co(1)–O(4)	2.252(3)
N(5)–Co(1)–N(3)	97.04(14)	N(5)–Co(1)–O(2)	155.51(13)
N(3)–Co(1)–O(2)	104.99(13)	N(5)–Co(1)–N(1)	98.12(14)
N(3)–Co(1)–N(1)	91.66(14)	O(2)–Co(1)–N(1)	91.91(14)
N(5)–Co(1)–O(1)	98.01(12)	N(3)–Co(1)–O(1)	163.71(13)
O(2)–Co(1)–O(1)	59.11(12)	N(1)–Co(1)–O(1)	92.37(13)
N(5)–Co(1)–O(4)	87.72(14)	N(3)–Co(1)–O(4)	96.87(14)
O(2)–Co(1)–O(4)	79.24(13)	N(1)–Co(1)–O(4)	169.03(13)
O(1)–Co(1)–O(4)	77.56(13)		
Complex **2**			
Cd(1)–N(3)	2.306(4)	Cd(1)–N(1)	2.306(4)
Cd(1)–N(5)	2.328(4)	Cd(1)–O(1)	2.430(4)
Cd(1)–O(5)	2.453(4)	Cd(1)–O(4)	2.470(4)
N(3)–Cd(1)–N(1)	92.97(15)	N(3)–Cd(1)–N(5)	97.18(13)
N(1)–Cd(1)–N(5)	169.76(15)	N(3)–Cd(1)–O(1)	130.55(13)
N(1)–Cd(1)–O(1)	82.26(15)	N(5)–Cd(1)–O(1)	90.08(14)
N(3)–Cd(1)–O(5)	93.23(13)	N(1)–Cd(1)–O(5)	95.29(15)
N(5)–Cd(1)–O(5)	85.51(14)	O(1)–Cd(1)–O(5)	136.17(13)
N(3)–Cd(1)–O(4)	144.69(14)	N(1)–Cd(1)–O(4)	87.62(15)
N(5)–Cd(1)–O(4)	84.89(13)	O(1)–Cd(1)–O(4)	84.53(14)
O(5)–Cd(1)–O(4)	51.64(13)		

2.7. Nonlinear optical measurements

The DMF solution of complexes **1** and **2** was placed in the 1 mm quartz curette, respectively, and the NLO properties were measured as described in the literatures [5,8,14–16,19].

2.8. Determination of TG-DSC

TG-DSC measurements were performed by heating the sample from 30 to 1100 °C for complex **1** or 30 to 900 °C for complex **2** at a rate of 10 °C min^{-1} in air on a Perkin–Elmer DTA-7 differential thermal analyzer.