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Research paper

Different structures of two Cu(I) complexes constructed by bridging 2,2-(1,4-butanediyl)bis-1,3-benzoxazole ligand: Syntheses, structures and properties

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ABSTRACT

Reaction of 2,2-(1,4-butanediyl)bis-1,3-benzoxazole (BBO) ligand with $[Cu(CH_3CN)_2(PPh_3)_2][X]$ ($X = ClO_4$, PF_6) afforded a copper(I) coordination polymer (CP) $\{[Cu(BBO)(PPh_3)]\cdot ClO_4\}_\infty$ (**1**) and a binuclear complex $[Cu_2(BBO)(PPh_3)_4]\cdot 2PF_6\cdot 2CH_2Cl_2$ (**2**) (where PPh_3 = triphenylphosphine). Two complexes have been characterized. The structural analysis revealed that in complexes **1**–**2**, all Cu(I) ions are tri-coordinated and the geometric structure around the central Cu(I) atom can be described as planar trigonal configuration. Complex **1** exhibits a one-dimensional coordination polymer by two BBO bridging adjacent copper(I) ions and extending along the b axis, forming a single-stranded helix chain structure that extends into 2-D layer frameworks through $\pi\cdots\pi$ interactions. Complex **2** shows a binuclear structure and the unit extends to a 2D supramolecular layered framework through C-H⋯F interactions. Moreover, compared with emissive bands of the free ligand in the solid state, the photoluminescent transition of the Cu(I) complexes **1**–**2** may be attributed to metal-to-ligand charge-transfer [MLCT].

1. Introduction

Benzoxazole is a five-membered ring compound containing both nitrogen and oxygen fused to a benzene ring and the benzoxazole ring is one of the most common heterocyclics in medicinal chemistry [1]. The binding force of metal ions with N and O atoms is different. In general, N-donor azole groups have shown strong coordination ability to the first-row transition metal ions [2]. P-containing ligands have large steric hindrance and rigid structure, which is beneficial to reduce the structural deformation of Cu(I) complexes, and the unique electronic effect of the P atoms can stabilize the copper(I) [3]. Accordingly, in order to enhance the phosphorescence intensity of copper(I) complexes, the usually-used N-containing heterocyclic ligands and phosphine ligands are simultaneously coordinated [4]. N-containing heterocyclic ligands, due to the diversity of coordination modes and configurations, are typically used as neutral ligands in the synthesis of complexes [5]. The counterions are introduced to balance the charge when studying the neutral ligand, which not only affect the coordination environment of the metal ions, but also the overall structure of the complex [6].

Copper(I), with a d^{10} electronic configuration, is well known for its tetrahedral coordination geometry, which is linked by two or four bridging ligands, leading to regular 1D chains, 2D layers, or 3D frameworks. Examples of the Cu(I) atoms adopting a 3-coordinate trigonal environment [7], afforded unprecedented structural motifs, such as 3D frameworks with rectangular extended channels or interwoven honeycombs. The observations clearly indicate the important role of coordination preferences in the determination of the architectures. The construction of copper(I) complexes containing triphenylphosphine and heterocyclic nitrogen ligands has drawn much attention in recent years, due to their interesting optical properties [8], as well as potentially-widespread applications in materials science, catalysis, synthetic and medicinal chemistry [9]. The selection of N-heterocyclic chelating ligand is paramount because, with it, copper(I) complexes possess high stability to promote luminescence from metal-to-ligand charge transfer (MLCT) and long fluorescence lifetime [10].

Helical structures have attracted an intense interest in coordination chemistry not only for their ubiquitous appearance in nature, a typical example being the DNA molecule, but also for their practical implications in multidisciplinary areas, such as structural biology, optical devices and biomimetic chemistry [11]. Until now, many single-, double-, triple-, and even multiple-stranded helices as well as circular and cylindrical helices have been prepared and comprehensively discussed. To get such helices, the crucial step

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is to choose multifunctional organic ligands containing appropriate coordination sites linked by a proper spacer with specific positional orientation.

On the basis of the above considerations, in this paper, a N-heterocyclic chelating bisbenzoxazole ligand combined with the second ligand triphenylphosphine and copper(I) salt was employed to obtain two copper(I) complexes. The structures of the two complexes have been characterized by elemental analysis, IR and X-ray single crystal diffraction. In addition, the luminescence and thermal stabilities properties have been studied.

2. Experimental section

2.1. Materials and general methods

All the chemicals and solvents were reagent grade and were used without further purification. ^{1}H NMR spectra were recorded on a Varian VR400 MHz spectrometer with TMS as an internal standard. Melting points were detected on an X-4 digital micro melting-point apparatus. The C, H and N elemental analyses were determined using a Carlo Erba 1106 elemental analyzer. The IR spectra were recorded in the 4000–400 cm^{-1} region with a Nicolet FT-VER-TEX 70 spectrometer using KBr pellets. Fluorescence spectral data were obtained on a 970-CRT fluorescence spectrophotometer at room temperature. Thermogravimetric analysis (TGA) was carried out on METTLER TOLEDO TGA1 thermal analyzer from room temperature to 800 °C with a heating rate of 10 °C/min under N_2 atmosphere.

2.2. Syntheses of the ligand and complexes

2.2.1. Synthesis of BBO

O-aminophenol (8.73 g, 0.08 mol), adipic acid (5.85 g, 0.04 mol) and 140 mL of polyphosphoric acid (PPA) were mixed and transferred into a 500 mL three-necked bottle. The mixture was stirred at 200 °C for 6 h. Thereafter, the resulting solution was cooled to 120 °C and poured into ice-water and 10% NaOH solution was used to adjust its pH to 10 after which a lot of pink precipitation was collected by filtration, washed with water and dried under vacuum. The crude product was recrystallized from ethanol to obtain white solids of BBO. Yield: 89%, m.p: 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65–7.67 (m, 2H, Ph-H), 7.44–7.47 (m, 2H, Ph-H), 7.65–7.67 (m, 4H, Ph-H), 2.99–3.03 (m, 4H, CH_2), 2.04–2.07 (m, 4H, CH_2). Anal. Calcd (%) for $C_{18}H_{16}N_2O_2$: C 73.95, H 5.52, N 9.58. Found: C 73.87, H 5.46, N 9.49. IR (KBr pellet, ν/cm^{-1}): 3051 (w), 2947 (w), 1609 (m), 1572 (s), 1453 (s), 1381 (m), 1246 (s), 943 (m), 831 (w), 746 (s).

2.2.2. Preparation of complexes

Two complexes were prepared using a similar procedure. CH_2Cl_2 solution (12 mL) of BBO (58.4 mg, 0.2 mmol) and copper(I) salt (0.1 mmol: $[Cu(CH_3CN)_2(PPh_3)_2]ClO_4$, 77 mg; $[Cu(CH_3CN)_2(PPh_3)_2]PF_6$, 81.5 mg) were stirred at ambient temperature for 4 h to give a colorless solution. The solvent was then removed at reduced pressure. The resultant residue was again dissolved in 5 mL CH_2Cl_2, and there was a slow diffusion of hexane into the above solution. Colorless crystals suitable for X-ray diffraction studies were obtained after 5 days.

Complex **1**. (72% yield). Anal. Calcd (%) for $C_{36}H_{31}ClCuN_2O_6P$: C 60.3, H 4.35, N 3.90. Found: C 59.8, H 4.11, N 3.78. IR (KBr pellet, ν/cm^{-1}): 3054 (w), 1554 (m), 1434 (w), 1246 (m), 1090 (s), 747 (m), 695 (m), 505 (w).

Complex **2**. (80% yield). Anal. Calcd (%) for $C_{46}H_{40}Cl_2CuF_6NOP_3$: C 57.3, H 4.18, N 1.45. Found: C 57.26, H 4.15, N 1.41. IR (KBr pellet, ν/cm^{-1}): 3054 (w), 1558 (m), 1479 (w), 1434 (w), 1246 (m), 1095 (w), 837 (s), 746 (m), 694 (m), 513 (w).

2.3. X-ray crystallography

Crystallographic data of complexes **1**–**2** were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296 K. Data reduction and cell refinement were performed using the SMART and SAINT programs [12]. The absorption corrections are carried out by the empirical method. The crystal structures of **1**–**2** were solved by direct methods and refined by full-matrix least-squares against F^2 of data using SHELXTL program [13]. The crystals of compound 1 are susceptible to weathering, resulting in the disorder about the uncoordinated ClO_4^- ion and a high wR_2 value. All non-hydrogen atoms were refined by using anisotropic thermal parameters. All hydrogen atoms were included in the calculated position and refined with the isotropic thermal parameters riding on the parent atoms. Crystal parameters and details of the final refinement parameters are shown in Table 1. The selected bond lengths and bond angles for complexes **1**–**2** are listed in Table 2.

3. Results and discussion

3.1. Characterization of the complexes

The synthetic routes to Cu(I) complexes are shown in Scheme 1. The elemental analysis of complexes **1**–**2** is in good agreement with the theoretical compositions. The free ligand is soluble in organic solvents but insoluble in water. The Cu(I) complexes are remarkably soluble in polar aprotic solvents such as DMF, DMSO, dichloromethane and acetonitrile, slightly soluble in ethanol and methanol, and insoluble in water, diethyl ether, petroleum ether and hexane.

3.2. X-ray structures of the complexes

3.2.1. Crystal structure of 1

Single-crystal X-ray diffraction analysis reveals that the asymmetric unit consists of one copper(I) ion, one BBO ligand, one triph-

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

Complex	1	2
Empirical formula	$C_{36}H_{31}ClCuN_2O_6P$	$C_{92}H_{80}Cl_4Cu_2F_{12}N_2O_2P_6$
Molecular weight	717.59	1928.28
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*P2(1)/c*
a (Å)	10.627(6)	10.6838(6)
b (Å)	10.696(6)	22.7066(13)
c (Å)	16.733(13)	19.0226(11)
α (°)	91.775(14)	90
β (°)	93.851(13)	103.1610(10)
γ (°)	119.079(9)	90
V (Å^3)	1654.2(18)	4493.5(4)
Z	2	2
D_{calcd} (g/cm^3)	1.44	1.425
μ (mm^{-1})	0.839	0.773
F(0 0 0)	740	1972
Total reflections	8161	23634
Unique reflections	5518	8359
R_{int}	0.0434	0.0236
GOF on F^2	1.032	1.019
R_1 ($I > 2\sigma(I)$)	0.0769	0.0375
wR_2 ($I > 2\sigma(I)$)	0.2044	0.0922
R_1 (*all data*)	0.1465	0.0518
wR_2 (*all data*)	0.2614	0.0997
$\Delta\rho$max, eÅ^{-3}	1.195	0.444
$\Delta\rho$min, eÅ^{-3}	−0.835	−0.670