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Six- and four-coordinated zinc(II) complexes exhibit strong blue fluorescent properties

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Abstract

A new ligand, 4-(*p*-chlorophenyl)-1,2,4-triazole (^{p}Cltrz), and its complexes, [Zn(^{p}Cltrz)$_6$]$_2$(ClO$_4$)$_2$ · H$_2$O (**1**) and [Zn(^{p}Cltrz)$_2$Cl$_2$] (**2**), were synthesized. The structure of **1** exhibits the first case that zinc(II) ion coordinated with six triazole ligands to form octahedral environment. Both **1** and **2** display very strong blue photoluminescence as the result of the fluorescence from the intraligand emission excited state.

Keywords: Zinc complex; Triazole; Crystal structure; Fluorescence properties

1. Introduction

In the past two decades, a variety of coordination compounds containing N^4 substituted 1,2,4-triazoles as ligands coordinated to metal ions have been reported [1–10]. By blocking the N^4 donor position through substitution, only the N^1 monodentate and the N^{1}N^2-didentate coordination modes are possible. Structures and properties of mono- and polynuclear compounds have been described [5–8,10]. On the other hand, blue luminescent metal complexes have been of our particular interest because they are one of the key color components required for full-color electroluminescent displays [11–13]. However, there are relatively few reports on the luminescent properties of triazole coordination compounds. In this present contribution, we synthesized a new N^4 substituted 1,2,4-triazole ligand (^{p}Cltrz = 4-(*p*-chlorophenyl)-1,2,4-triazole), and obtained two zinc(II) complexes, namely [Zn(^{p}Cltrz)$_6$](ClO$_4$)$_2$ · H$_2$O (**1**) and [Zn(^{p}Cltrz)$_2$Cl$_2$] (**2**). Both X-ray crystal structures and their strong blue luminescent properties form the subject of this communication.

2. Experimental

2.1. *Synthesis*

The new ligand ^{p}Cltrz was synthesized using a method similar to that reported by Bayer et al. for the preparation of other 4-substituted-1,2,4-triazoles [14]. In this case 4-chloroaniline (1 mol) was added slowly to the boiling solution of monoformylhydrazine (1 mol) and triethylorthoformate (1.5 mol) in 400 ml of anhydrous methanol. The solution was refluxed for 4 h and the solvent was then removed under reduced pressure. After cooling to room temperature, the solid was washed with a little hexane, and then washed three times with tetrahydrofuran. A snow-white powder was yielded (48%). $W = 179.5$; m.p.: 130–133 °C; IR (cm^{-1}): 3120(s), 1600 (s), 1525(vs), 1420(s), 1370(vs), 1240(vs), 1090(vs), 865 (s), 825(vs), 738(s), 630(s). Anal. Calc. for C$_8$H$_6$N$_3$Cl: C, 53.48; H, 3.34; N, 23.40%; Found: C, 53.56; H, 3.20; N, 23.21%.

A solution of the Zn(ClO$_4$)$_2$ · 6H$_2$O (0.1 mmol) or ZnCl$_2$ (0.1 mmol) was dropped into a vigourously stirred solution of the ligand (0.4 mmol). Stirring was continued for a given amount of time. Then the solution was filtered and reduced in volume in vacuo until the complex started to precipitate. Then the reaction flask

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was kept at 0 °C for 3 days. The colorless crystalline products suitable for X-ray structure analysis were gradually formed in the solution. Anal. Calc. for $C_{48}H_{38}Cl_8N_{18}O_9Zn$ (**1**): C, 42.36; H, 2.79; N, 18.53%; Found: C, 42.10; H, 2.82; N, 18.45%. m.p.: 235–237 °C. Anal. Calc. for $C_{16}H_{12}Cl_4N_6Zn$ (**2**): C, 38.75; H, 2.42; N, 16.95%; Found: C, 38.62; H, 2.50; N, 16.80%. m.p.: 217–219 °C.

2.2. *Physical measurements*

All the solvents and chemicals were reagent grade and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin–Elmer analyzer model 240. Infrared spectra were measured on a Bruker Vector 22 FT-IR instrument from KBr pellets. Diffuse reflectance absorption spectrum was performed with a Shimadzu UV-2101PC spectrophotometer in the range of 200–2000 nm at room temperature. The photoluminescence spectrum was measured by MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source.

2.3. *Crystal structure determination*

Crystal data for **1**: $C_{48}H_{38}Cl_8N_{18}O_9Zn$, $M = 1359.93$, monoclinic, $P2_1/c$, $a = 20.369(12)$, $b = 14.773(8)$, $c = 20.416(12)$ Å, $\beta = 113.675(8)°$, $V = 5627(6)$ Å^3, $Z = 4$, $D_c = 1.605$ g/cm^3, $R_1 = 0.0447$, $wR_2 = 0.0988$ $(I > 2\sigma(I))$; $R_1 = 0.1010$, $wR_2 = 0.1345$ (for all data), and $S = 0.898$. Crystal data for **2**: $C_{16}H_{12}Cl_4N_6Zn$, $M = 495.49$, monoclinic, $P2_1/c$, $a = 14.892(5)$, $b = 18.594(7)$, $c = 7.147(2)$ Å, $\beta = 99.000(6)°$, $V = 1954.7(11)$ Å^3, $Z = 4$, $D_c = 1.684$ g/cm^3, $R_1 = 0.0423$, $wR_2 = 0.0864$ $(I > 2\sigma(I))$; $R_1 = 0.0959$, $wR_2 = 0.1297$ (for all data), and $S = 0.900$. X-ray diffractions were collected on a BRUKER SMART 1000 CCD detector with graphite-monochromatized Mo-Kα radiation with radiation wavelength 0.71073 Å at 293(2) K. The structures were solved by direct-methods using the program SHELXS-97 [15] and Fourier difference techniques, and refined by full-matrix least-squares method on F^2 using SHELXL 97 [16].

3. Results and discussion

Two zinc salts, $Zn(ClO_4)_2 \cdot 6H_2O$ as species with non-coordinating anions and $ZnCl_2$ as species with coordinating anions, were chosen for the reactions with ^{p}Cltrz. The structures of **1** and **2** have shown that the coordinative behaviour of the anions was as expected [17].

The cationic unit of **1** is depicted in Fig. 1. The zinc(II) ion in **1** is located on a slightly distorted octahedral center relating six N-donating ^{p}Cltrz ligands. The Zn–N (2.132(4)–2.221(4) Å) distances are within the range observed for other octahedral complexes [17]. The N(13)–Zn(1)–N(4), N(13)–Zn(1)–N(16) and N(13)–Zn(1)–N(10) angles are 176.51(14), 90.01(14) and 90.32 (14)°, respectively, indicating a slight distortion. It is noticeable that there is a considerable variation in the Zn–N distances around the metal ion and Zn(1)–N(13) bond length is almost 0.09 Å shorter than Zn(1)–N(7) distance, this may be due to the need to 'ease' the space repulsion of the triazole ligands. Through a few mononuclear compounds are known in which the 4-substituted triazole coordinates through N1 [17–20], this is the first example that metal ion coordinated via six triazole ligands. The ORTEP of **2** is shown in Fig. 2 together with the atomic labeling scheme. The coordination sphere of the Zn(II) ion may be described as a slightly distorted tetrahedron. The metal ion in **2** is coordinated by two nitrogen atoms of two triazole ligands and two chloride atoms. The Zn–N bond lengths are very close to each other with the average value of 2.018 Å. The Zn–Cl distances are 2.2039 (17) and 2.2352 (18) Å, respectively. The bond angles around the zinc atom deviate much with respect to the value expected for an ideal tetrahedron, 109.4°. Compared with **1**, the dihedral angle between phenyl ring and triazole ring of the ^{p}Cltrz ligand is almost 4° bigger in compound **2**, this may attribute to the space repulsion ligands in **1**.

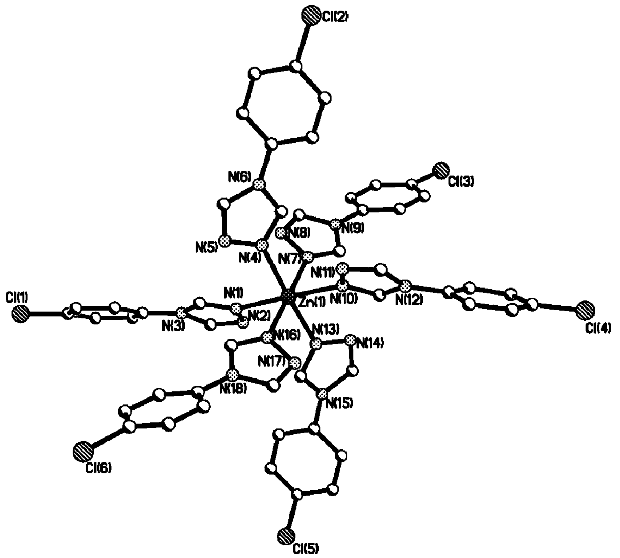

Fig. 1. The ORTEP drawing of $[Zn(^{p}Cltrz)_6]^{2+}$. Selected interatomic bond distances (Å) and angles (°): Zn(1)–N(13) 2.132(4), Zn(1)–N(4) 2.156(4), Zn(1)–N(10) 2.175(3), Zn(1)–N(16) 2.177(4), Zn(1)–N(7) 2.202(4), Zn(1)–N(1) 2.221(4), N(13)–Zn(1)–N(4) 176.51(14), N(13)–Zn(1)–N(10) 90.32(14), N(13)–Zn(1)–N(16) 90.01(14), N(16)–Zn(1)–N(7) 179.17(14), N(13)–Zn(1)–N(7) 90.72(14), N(10)–Zn(1)–N(16) 89.15(14), N(13)–Zn(1)–N(1) 88.06(14).

The excitation and emission spectra of pure **1**, **2** and ^{p}Cltrz in the DMF solution with the same concentration at room temperature are shown in Fig. 3. The very strong blue fluorescence for the two complexes can be

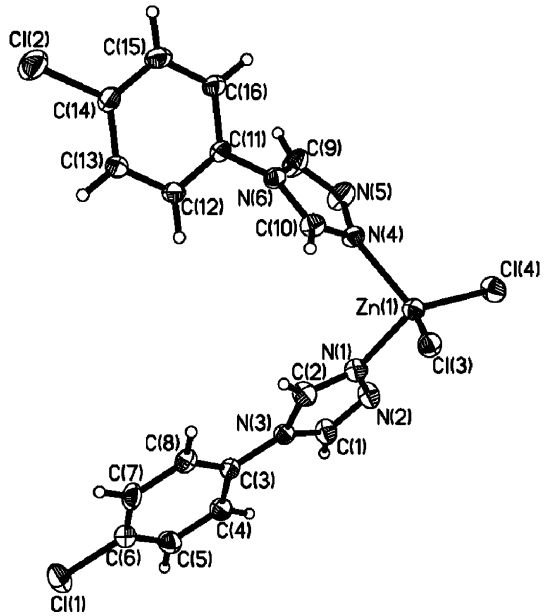

Fig. 2. The ORTEP drawing of [Zn(^{P}Cltrz)$_2$Cl$_2$]. Selected interatomic bond distances (Å) and angles (°): Zn(1)–N(1) 1.998(5), Zn(1)–N(4) 2.039(5), Zn(1)–Cl(4) 2.2039(17), Zn(1)–Cl(3) 2.2352(18), N(1)–Zn(1)–N(4) 99.21(19), N(1)–Zn(1)–Cl(4) 114.70(15), N(4)–Zn(1)–Cl(4) 114.66(14), N(1)–Zn(1)–Cl(3) 103.60(14), N(4)–Zn(1)–Cl(3) 103.33(15), Cl(4)–Zn(1)–Cl(3) 118.83(7), C(2)–N(1)–Zn(1) 131.0(4), N(2)–N(1)–Zn(1) 121.3(4), N(5)–N(4)–Zn(1) 125.2(4).

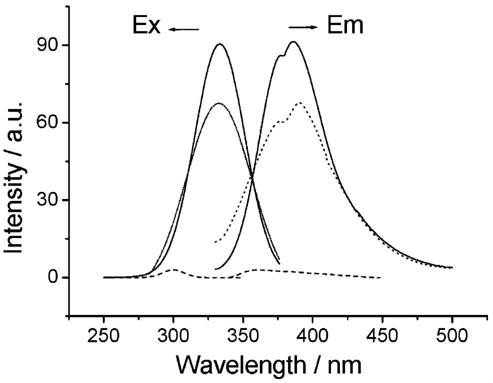

Fig. 3. The excitation and emission spectra of pure **1**, **2** and ^{P}Cltrz in the DMF solution at room temperature (**2**, solid line; **1**, dot line; ^{P}Cltrz, dash line).

observed, where the maximum emission wavelength at 383 nm for **1** and 381 nm for **2**. Additional shoulder peaks at 373 nm for **1** and 375 nm for **2** also can be detected. The emission of the two complexes is due to the fluorescence from the intraligand emission excited state. Correspondingly, the broad peak with the maximum excited light at ca. 330 nm can be observed both in the exciting spectra for the two complexes. Contractively, the free neutral ligand ^{P}Cltrz displays very weak emission at 359 nm in the UV region, in corresponding to the excited light at 300 nm. The enhanced fluorescence efficiency of the complexes is attributed to the coordination of the ^{P}Cltrz ligand to the zinc(II) ion that effectively increases the rigidity of the ligand and reduces the loss of energy via radiationless thermal vibrations. The condensed structures for the two complexes are also an attribution. The red shift of the emission from the UV light region to the blue color region is complicated. Compared with two compounds, the structures are different, while the emission behavior is similar. Thus, it should be concluded that the dominated factor be due to the coordination of ligand to metal ion. From the experiment we can see that the fluorescence efficiency for **2** is higher than that for **1**. The reason for this may be due to the energy difference in zinc ion caused by the coordination environment. The high luminescence efficiency in blue light region as well as the high thermally stability indicates the two complexes may be excellent candidate for highly thermally stable blue fluorescent materials.

In summary, we have successfully synthesized a new triazole ligand and two Zn(II) complexes. **1** is the first example that metal ion coordinated by six triazole ligands in mononuclear compounds. Both **1** and **2** show strong blue photoluminescence as the result of the fluorescence from the intraligand emission excited state. Efforts to further investigate other luminescent metal complexes and synthesized novel ligands are underway in our laboratory.

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