Blue Luminescent Zn(II) and Hg(II) Complexes with 2-[4-(Dimethylamino)styryl]pyridine; Structural and Luminescent Properties

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Received October 1, 2009. Accepted October 20, 2009

Key Words: Zn(II) complex, Hg(II) complex, 2-[4-(Dimethylamino)styryl]pyridine complex, Luminescence, Intra-ligand charge transfer compound

Luminescent organic and metal coordination compounds have attracted considerable attention for their potential applications in electroluminescent displays. Among coordination compounds, chelate d10 metal complexes are of great interest due to their high thermal stability and low cost as well as their good photoluminescent and electroluminescent properties. For example, Zn(II) complexes with nitrogen and oxygen donor atoms exhibit blue or white emissions. Meanwhile, less luminescent Hg(II) complexes have been reported. Recently some coordination polymers Hg(II) complexes have shown blue fluorescence originating from intra-ligand charge transfer (ILCT) transitions. Herein, two novel d10 metal (M = Zn and Hg) complexes with 2-[4-(dimethylamino) styryl]pyridine (dmasp) were prepared and their structural and luminescent properties were investigated. The dmasp ligand was of interest as it had an electron push-pull system, thereby stabilizing the π* levels and, in them, ILCT transitions could arise readily through a conjugated π system, which is also important to ILCT photoluminescent materials as well as the second-order nonlinear optical (NLO) materials.

Experimental

Synthesis of Zn(dmasp)Cl2 (1). To a stirred solution of 2-[4-(dimethylamino)styryl]pyridine (449 mg, 2.0 mmol) in methanol (15 mL) was added with a solution of ZnCl2 (272 mg, 2.0 mmol) in water (5 mL). The reaction mixture was stirred for 12 hr at room temperature. After filtering, the yellow precipitate was collected. Light yellow crystals of 1 were obtained by slow evaporation in a dichloromethane solution. Elemental analyses were performed at the Korea Basic Science Institute. Yield 932 mg (79.7%). mp: 242 °C. Anal. Calc. for C18H23N2Cl2Zn (Zn(dmasp)Cl2): C, 61.60; H, 5.51; N, 9.58. Found: C, 61.33; H, 4.98; N, 9.37. 1H NMR (6 ppm, d6-DMso): 298 K: δ = 8.46 (d, 2H, J = 4.2 Hz), 7.70 (t, 2H, J = 7.8 Hz), 7.47 (m, 8H), 7.15 (t, 2H, J = 4.2 Hz). 7.00 (d, 2H, J = 15.9 Hz), 6.71 (d, 4H, J = 8.4 Hz), 2.92 (s, 12H). Synthesis of Hg(dmasp)Cl2 (2). Hg(dmasp)Cl2 was prepared and its yellow crystals were obtained by a similar method of Zn analogue using HgCl2. Yield 1256 mg (87.2%). mp: 159 °C. Anal. Calc. for C18H23N2Cl2Hg (Hg(dmasp)Cl2): C, 50.04; H, 4.48; N, 7.78. Found: C, 49.89; H, 4.33; N, 7.69. 1H NMR (δ ppm, d6-DMSO, 298 K): δ = 8.48 (d, 2H, J = 4.8 Hz), 7.71 (t, 2H, J = 7.8 Hz), 7.51 (m, 8H), 7.16 (t, 2H, J = 4.8 Hz), 7.02 (d, 2H, J = 15.9 Hz), 6.71 (d, 4H, J = 8.7 Hz), 2.93 (s, 12H).

Instruments. The 1H-NMR spectra were recorded with a Varian Mercury 300 spectrometer with CDCl3 (δ = 7.27 ppm) as an internal reference. The absorption (UV-Vis) and photoluminescence (PL) spectra were measured by a Jasco V-570 UV-Vis spectrophotometer, and a Hitachi F-4500 fluorescence spectrophotometer, respectively. From 200 to 800 nm. Cyclic voltammetry (CV) experiments were performed on a Bioanalytical Systems CVS-50W voltammetric analyzer in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu4NBF4). The Pt disk electrode, Ag/AgNO3 (0.1 M) electrode and Pt electrode were used as the working, reference and counter electrodes, respectively, at a scan rate of 100 mVs-, and ferrocene was used as a reference. Thermal analyses were carried out on a Metler Toledo TGA/STA 801 analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min.

Crystallography. X-ray intensity data were collected at room temperature on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Structure was solved by applying the direct method using a SHELXS-97 and refined by a full-matrix least-squares calculation on F² using SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and were riding on their respective carbon atoms (Eiso = 1.2 Eo and 1.5 Eo). Crystal data for 1: C18H23N2Cl2Zn, M = 584.87, Monoclinic, P21/c, a = 14.108(2), b = 9.4890(16), c = 21.606(4), β = 99.930(3)°, Z = 4, Dc = 1.363 Mg m-3, μ = 1.075 mm-1, F(000) = 2750, 23572 reflections (Rint = 0.0667), 6544 unique reflections, 333 parameters refined. GOF = 1.061, Final R indices [I > 2σ(I)], R1 = 0.0561, wR2 = 0.1411, all data: R1 = 0.1202, wR2 = 0.1844. Crystal data for 2: C18H23N2Cl2Hg, M = 720.09, Monoclinic, P21/c, a = 9.5858(3), b = 11.7419(3), c = 13.2808(4), γ = 97.219(9)°, β = 71.767(7), γ = 88.966(8), Z = 4, Dc = 1.690 Mg m-3, μ = 5.624 mm-1, T(000) = 260.00, 24342 reflections (Rint = 0.0499), 5574 unique reflections, 334 parameters refined. GOF = 1.004, Final R indices [I > 2σ(I)], R1 = 0.0396, wR2 = 0.0862, all data: R1 = 0.0676, wR2 = 0.0990.
Results and Discussion

Zn(dmasp)$_2$Cl$_2$ (1) and Hg(dmasp)$_2$Cl$_2$ (2) were obtained from the reaction of metal chloride with dmasp ligand in methanol at room temperature.

![Figure 1. ORTEP diagram of 1 (ellipsoids with 30% probability). Selected bond lengths (Å) and bond angles (°) for 1: Zn-N1 2.079 (3), Zn-N2 2.071(4), Zn-Cl1 2.234(13), Zn-Cl2 2.2527(13), N1-Zn-N2 101.70(14), N1-Zn-Cl1 116.1(10), N1-Zn-Cl2 106.24(10), N2-Zn-Cl1 105.26(11), N2-Zn-Cl2 117.13(11), Cl1-Zn-Cl2 115.47(5).](image1)

The thermal stability, investigated using thermal gravimetric analysis (TGA), showed that the 5% weight decomposition temperatures were 273 and 216 °C for 1 and 2, respectively, showing high thermal stability as would be required for use in an electroluminescent device.

Single crystals were obtained by slow evaporation from a dichloromethane solution, producing light yellow crystals. ORTEP views of complexes 1 and 2, including the numbering scheme, are shown in Figures 1 and 2, respectively. In both complexes, the metal atoms were coordinated with two nitrogen atoms of the dmasp ligands and two chloride atoms. The bond angles around the metal atoms were in the range of 101.7 - 117.2° for 1 and 97.5 - 121.3° for 2, suggesting the coordination geometry as a distorted tetrahedral centered on the metal atom. The dihedral angle between the N1-M-N18 and Cl1-M-Cl2 planes were 82.0(10)° and 77.67(11)° for 1 and 2, respectively, which was close to 90° for the perfect tetrahedron. The dmasp ligand is a conjugated system and all included heavy atoms are nearly coplanar. In both complex 1 and 2, the two coordinated ligands on the metals were almost perpendicular to each other, with the dihedral angle between two dmasp ligands at 86.1(1)° and 82.6(1)° for the Zn(1) and Hg(2) complexes, respectively.

In complex 1, the average Zn-N distance [2.075(4) Å] was shorter than reported Zn-N bond lengths ranging from 2.1 - 2.2 Å and the average Zn-Cl bond lengths [2.371(13) Å] were similar to reported values.5 The average Hg-N [2.339(5) Å] and Hg-Cl bond distance [2.420(3)(16) Å] in 2 were similar to reported values.

The intermolecular distance between the two parallel dmasp ligands N18-C31 and C31'-N18' [symmetry code: (i) -x+2, -y+1, and -z] in the packing structure of the Zn complex (1) was 3.5 Å, which indicated the existence of significant π-π interactions and, in complex 2, this intermolecular distance was 3.5 Å. The molecular packing diagrams are shown in Figure 3.

![Figure 2. ORTEP diagram of 2 (ellipsoids with 30% probability). Selected bond lengths (Å) and bond angles (°) for 2: Hg-N1 2.315(5), Hg-N18 2.362(5), Hg-N18 2.360(15), Hg-Cl2 2.225(17), N1-Hg-N2 97.5(16), N1-Hg-Cl1 120.85(12), N1-Hg-Cl2 101.74(13), N2-Hg-Cl1 99.04(13), N2-Hg-Cl2 114.57(13), Cl1-Hg-Cl2 121.10(6).](image2)

![Figure 3. The molecular packings for complexes 1 (a) and 2 (b).](image3)

The absorption and photoluminescence spectra in chloroform showed a strong absorption by the free dmasp ligand at 359 nm, assigned to the intraligand (IL) π-π$^*$ transition, and complexes 1 and 2 exhibited a 9 nm red shift compared with the free ligand (Figure 4 and Table 1). The absorption intensity of complexes 1 and 2 was stronger than the free ligand, supporting that the metal ion played a role in stabilizing the ligand in the complex.

Both the ligand and complexes 1 and 2 in chloroform displayed a broad, featureless emission band with maximum intensities at ~450 nm upon 370 nm excitation. The PL quantum yield (Φ) of the complexes was measured in chloroform versus 9,10-diphenylanthracene and was determined to be 3.9% and 3.7% for 1 and 2, respectively, and similar to dmasp (3.5%).
The similarity of the emission peaks of complexes 1 and 2 to the free ligand led to the conclusion that the emissions could be attributed to intraligand charge transfer (ILCT) transitions, a conclusion supported by the fact that the fluorescence showed a large solvent effect. With increasing solvent polarity, the emission wavelengths were found to increase significantly. The Lippert-Mataga plot in a variety of solvents is shown in Figure 5. It showed a significant positive solvatochromism of the emission maximum as a function of the solvent polarity, resulting from the contribution of the solvent reorientation energy. It is thought that ILCT transitions in the dmasp ligand arise from the electron-donor dimethylamino substituent donating to the electron-acceptor pyridine ring via the π-linker styryl group. The coordination to the metal was expected to enhance the electron-acceptor capability of the pyridine ring as the π-conjugation system would be extended upon coordination and the emission peak moved to a lower frequency since the electron transition energy of ILCT decreased, and thus the π-π* energy gap decreased. A 4 - 5 nm bathochromic shift of the emissions was observed in complexes 1 and 2, compared with the free ligand.

In the solid state of complexes 1 and 2, the intermolecular π-π interactions between the monomeric units further extended the π-conjugation system and resulted in a ~ 90 nm bathochromic shift in the emissions from the complexes in the film state when compared with the solution state, as shown in Table 1. Face to face π-π interactions in the solid state would lead to a broad, featureless luminescence that is red-shifted compared to emissions in solution.

The electrochemical properties, as is shown in Figure 6, showed that both the ligand and complexes 1 and 2 in chloroform underwent an irreversible oxidation process in the range of 1.22 - 1.36 V, which was attributed to the oxidation of the ligand. From the obtained oxidation potential and the absorption edges of the UV-visible spectra, the HOMO and LUMO energy levels and the energy gaps (Eg) were calculated. The results are in Table 2. The Hg(II) complex showed a cathodic peak at 0.33 V, believed to the Hg(II)/Hg(II) process.

In conclusion, we prepared two blue, luminescent Zn(II) and Hg(II) chloride complexes with dmasp ligands. The complexes were stabilized from π-π interactions between the para-
Table 2: Electrochemical data, HOMO, LUMO and optical energy gap of dmnap and complexes 1 and 2

<table>
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<th>Complex</th>
<th>E&lt;sub&gt;pa&lt;/sub&gt; (mV)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>HOMO (eV)</th>
<th>Energy gap (eV)</th>
<th>LUMO (eV)&lt;sup&gt;b&lt;/sup&gt;</th>
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<sup>a</sup>Data were collected in chloroform containing 0.001 M complexes by cyclic voltammetry. <sup>b</sup>Data were collected in chloroform by UV-Vis spectrophotometer.

allel dmnap ligands in the solid state. The luminescent properties showed that the photoluminescence arise from the intraligand emission from the excited state, and that they are novel potential candidates for applications in optoelectronic devices.

Acknowledgments. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2006-521-C00083). X-ray data were collected at the center for Research Facilities in Chungnam National University.

Supplementary Data: Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition Nos. CCDC-635387 for Zn(dmnap):Cl<sub>2</sub> and CCDC-635389 for Hg(dmnap):Cl<sub>2</sub>). The data can be obtained free of charge via www.ccdc.cam.ac.uk/deposit (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-01223 336033; E-mail: deposit@ccdc.cam.ac.uk).

References


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