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

Hoe-Joo Seo, Jeong Sim Ryu, Ki-Sun Nam,[‡] Sung Kwon Kang,[†] Sun Young Park,[†] and Young-Inn Kim^{‡,†}

Department of Chemistry, Pusan National University, Pusan 609-735, Korea ^{*}Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea ^{*}Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials. Pusan National University, Pusan 609-735, Korea. ^{*}E-mail: yikim@pusan.ac.kr Received October 1, 2009, Accepted October 20, 2009

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

Luminescent organic and metal coordination compounds have attracted considerable attention for their potential applications in electroluminescent displays.¹ 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.² For example, Zn(II) complexes with nitrogen and oxygen donor atoms exhibit blue' and white emissions.4 Meanwhile, less luminescent Hg(II) complexes have been reported. Recently some coordination polymeric Hg(II) complexes have shown blue fluorescence originating from intraligand charge transfer (ILCT) transitions.⁵ Herein, two novel d^{10} metal ($M^{2+} = Zn^{2-}$ and Hg^{2-}) 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.^o

Experimental

Synthesis of Zn(dmasp)₂**Cl**₂ (1). To a stirred solution of 2-[4-(dimethylamino)styryl]prydine (449 mg, 2.0 mmol) in methanol (15 mL) was added with a solution of ZnCl₂ (272 mg, 2.0 mmol) in methanol (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 Korean Basic Science Institute. Yield 932 mg (79.7%). mp: 242 °C. Anal. Calcd. for C₃₀H₃₂N₄Cl₂Zn (Zn(dmasp)₂Cl₂): C. 61.60; H, 5.51; N. 9.58. Found: C. 61.33; H. 4.98; N. 9.37. ¹H NMR (δ , ppm; 6-DMSO, 298 K): 8.48 (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)₂Cl₂ (2). Hg(dmasp)₂Cl₂ 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. Calcd. for $C_{3c}H_{32}N_4Cl_2Zn$ (Hg(dmasp)₂Cl₂): C, 50.04; H. 4.48: N, 7.78. Found: C, 49.89: H. 4.33; N, 7.69. ¹H NMR (\hat{o} . ppm; 6-DMSO, 298 K): 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 (¹H: 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 CV-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 mV/s, and ferrocene was used as a reference. Thermal analyses were carried out on a Metler Toledo TGA/DTA 815 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 K α 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 F^2 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 (B_{180} = 1.2 B_{eq} and 1.5 B_{eq}). Crystal data for 1: C₃₀H₃₂Cl₂ $N_4Zn_1 M_w = 584.87$. Monoclinic, $P2_1/n_1 a = 14.108(2)$ Å, b =9.4890(16) Å, c = 21.606(4) Å, $\beta = 99.930(3)^{\circ}$, U = 2849.1(8) \dot{A}^3 , Z = 4, $D_{calc} = 1.363 \text{ Mg m}^3$, $\mu = 1.075 \text{ mm}^3$, $\theta_{max} = 27.50 \text{ °}$, 23572 reflections ($R_{int} = 0.0667$). 6544 unique reflections, 333 parameters refined. GOF = 1.061, Final *R* indices $[I \ge 2\sigma(I)]$: $R_1 = 0.0561$, $\omega R_2 = 0.1411$, all data: $R_1 = 0.1202$, $\omega R_2 = 0.1844$. Crystal data for 2: $C_{30}H_{32}$ Cl₂N₄Hg, M_w = 720.09. Triclinic, P.1, a = 9.5858(3) Å, b = 11.7419(3) Å, c = 13.2808(4) Å, a =87.219(8) °. β = 71.376(7) °. γ = 88.966(8) °. V = 1414.88(9) Å³. Z = 2, D_{cale} = 1.690 Mg m⁻³, μ = 5.654 mm⁻¹. θ_{max} = 26.00 °. 24342 reflections ($R_{int} = 0.0499$). 5457 unique reflections, 334 parameters refined. GOF = 1.004, Final *R* indices $[I \ge 2\sigma(I)]$: $R_1 = 0.0396$, $\omega R_2 = 0.0862$, all data: $R_1 = 0.0676$, $\omega R_2 = 0.0990$.

Results and Discussion

 $Zn(dmasp)_2Cl_2$ (1) and $Hg(dmasp)_2Cl_2$ (2) were obtained from the reaction of metal chloride with dmasp ligand in methanol at room temperature.



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 a electroluminescent device.⁷

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 chlorine atoms. The bond angles around the metal atoms were in the range of $101.7 - 117.2^{\circ}$ for 1 and 97.5 - 121.1° for 2, suggesting the coordination geometry as a distorted tetrahedral centered on the metal atom. The dihedral angle between the N1-M-N18 and C11-M-C12 planes were $82.01(10)^{\circ}$ and $77.67(11)^{\circ}$ for 1 and 2, respectively.



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 2.2414(13), Zn-Cl2 2.2327(13), N1-Zn-N2 101.70(14), N1-Zn-Cl1 116.16(10), N1-Zn-Cl2 106.24(10), N2-Zn-Cl1 105.26(11), N2-Zn-Cl2 117.13(11), Cl1-Zn-Cl2 110.47(5).



Figure 2. ORTEP diagram of 2 (ellipsoids with 30% probability). Selected bond lengths (Å) and bond angles (°) för 2; Hg-N1 2.315(5), Hg-N18 2.362(5), Hg-Cl1 2.4160(15), Hg-Cl2 2.4245(17), N1-Hg-N2 97.51(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).



(b)



Figure 3. The molecule packings for complexes 1 (a) and 2 (b).

tively, 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 Å⁸ and the average Zn-Cl bond lengths [2.2371(13) Å] were similar to reported values.⁵ The average Hg-N [2.339(5) Å]and Hg-Cl bond distance [2.4203(16) Å] in 2 were similar to reported values.^{10,11}

The intermolecular distance between the two parallel dmasp ligands N18-C31 and C31¹-N18¹ [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.

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, ¹² 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%). Notes



Figure 4. Absorption (A) and photoluminescence spectra of dmasp, complexes 1 and 2 in chloroform (B) $(1.0 \times 10^{-5} \text{ M})$ and film state (C).



Figure 5. A plot of the absorption and emission maxima of dmasp, complexes 1 and 2 as a function of solvent polarity parameter of the Lippert-Mataga model, where n and ε are the refractive index and dielectric constant of the solvent, respectively.

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.¹² With increasing solvent polarity, the emission wavelengths were found to increase significantly. The Lippert-Metaga plot¹³ 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.^{12,14} 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



Figure 6. The cyclic voltammograms of dmasp, complexes 1 and 2.

Table 1. Photophysical properties of dmasp and complexes 1 and 2

Complex	$\begin{array}{l} Absorption \ \lambda \ (nm)^a \\ (\epsilon, \times \ 10^3 \ M^1 \ cm^1) \end{array}$	$\begin{array}{c} Emission \lambda_{max} \\ (nm) \end{array}$		$\Phi\left(\% ight)^{b}$	Td (°C) ^c
		solution ^a	film	-	
dmasp	359 (20)	447	540	3.5	
1	368 (45)	452	540	3.9	273
2	368 (33)	451	540	3.7	216

^aMeasured in chloroform at room temperature. ^bExcitation wavelength was 370 nm. 9.10-Diphenylanthracene (0.91) was an external reference. ^c T_d is the decomposition temperature at 5% weight loss.

enhance the electron-acceptor capability of 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.¹⁵ 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.¹⁶

The electrochemical properties, as is shown in Figure 6, showed that both the ligand and complexes 1 and 2 in chloroform underwent a 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 (E_8) were calculated.¹⁷ The results are in Table 2. The Hg(II) complex showed a cathodic peak at -0.33 V, believed to the Hg(II)/Hg(I) process.¹⁸

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 par-

 Table 2. Electrochemical data, HOMO, LUMO and optical energy gap of dmasp and complexes 1 and 2

Complex	$E_{\mathrm{ex}}\left(mV\right)^{\alpha}$	HOMO (eV) ^o	Energy gap (eV) LUMO $(eV)^{b}$		
dmasp	1.22	5.96	2.58	3.38	
1	1.24	5.97	2.59	3.38	
2	1.36	6.09	2.79	3.31	

^aData were collected in chloroform containing 0.001M complexes by cyclic volammograms. ^bData were collected in chloroform by UV-Vis spectrophotometer.

allel dmasp ligands in the solid state. The luminescent properties showed that the photoluminescence arose 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(dmasp)₂Cl₂ and CCDC-635389 for Hg(dmasp)₂Cl₂). 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

- (a) Wang, S. Coord. Chem. Rev. 2001, 215, 79. (b) He, Z.; Wong, W.-Y.; Yu, X.; Kwok, H.-S.; Lin, Z. Inorg. Chem. 2006, 45, 10922. (c) Thoi, V. S.; Stork, J. R.; Magde, D.; Cohen, S. M. Inorg. Chem. 2006, 45, 10688. (d) Ghedini, M.; Deda, M. L.; Aiello, I.; Grisolia, A. Inorg. Chim. Acta 2004, 357, 33. (e) Song, J.-L.; Mao, J.-G. J. Mol. Struct. 2005, 740, 181. (f) Wong, W.-Y.; Tsang, K.-Y.; Tam, K.-H.; Lu, G.-L.; Sun, C. J. Org. Chem. 2000, 601, 237. (g) Xu, Y.; Chen, B.; Gong, Y.; Yuan, D.; Jiang, F.; Hong, M. J. Mol. Struct. 2006, 789, 220.
 (a) Wang, X.; Qin, C.; Wang, E.; Li, Y.; Hao, N.; Hu, C.; Xu, L.
- (a) Wang, X.; Qin, C.; Wang, E.; Li, Y.; Hao, N.; Hu, C.; Xu, L. *Inorg. Chem.* 2004, *43*, 1850. (b) Qin, C.; Wang, X.; Wang, E.; Xu, L. J. Mol. Struct. 2005, *738*, 91. (c) Wen, L.; Li, Y.; Dang, D.; Tian, Z.; Ni, Z.; Meng, Q. J. Solid State Chem. 2005, *178*, 3336. (d) Majumder, A.; Rosair, G. M.: Mallick, A.; Chattopadhyay, N.; Mitra, S. Polyhedron 2006, *25*, 1753. (e) Muthu, S.; Ni, Z.; Vittal, J. J. *Inorg. Chim. Acta* 2005, *358*, 595. (f) Yue, S.-M.; Xu, H.-B.; Ma, J.-F.; Su, Z.-M.; Kan, Y.-H.; Zhang, H.-J. Polyhedron 2006, *25*, 635.
- 3. (a) Song, Y.-S.; Yan, B.; Chen, Z.-X. Inorg. Chem. Commun.

2005, *8*, 1165. (b) Zhu, L.-N.; Zhang, L. Z.; Wang, W.-Z.; Liao, D.-Z.; Cheng, P.; Jiang, Z.-H.; Yan, S.-P. *Inorg. Chem. Commun.* **2002**, *5*, 1017. (c) Tandon, S. S.; Chander, S.; Thompson, L. K. *Inorg. Chim. Acta* **2000**, *300*, 6831. (d) Liu, S.-F.; Wu, Q.; Schmider H. L.: Aziz, H.: Hu, N.-X.; Popoyic, Z.; Wang, S. J.

- Schmider, H. L.: Aziz, H.: Hu, N.-X.; Popovic, Z.: Wang, S. J. Am. Chem. Soc. 2000, 122, 3671. (e) Klappa, J. J.: Geers, S. A.;
 Schmidtke, S. J.; MacManus-Spencer, L. A.; McNeill, K. Dalton Trans. 2004, 883. (f) Maxim, C.; Pasatoiu, T. D.; Kravtsov, V. C.; Shova, S.; Muryn, C. A.; Winpenny, R. E. P.; Tuna, F.; Andruh, M. Inorg. Chim. Acta 2008, 361, 3903. (g) Li, J.; Zhou, J.-H.; Li, Y.-Z.; Weng, L.-H.; Chen, X.-T.; Yu, Z.; Xue, Z. Inorg. Chem. Commun. 2004, 7, 538.
- (a) Hamada, Y.; Fujii, T.; Sano, H.; Nishio, Y.; Takahashi, H.; Shibata, K. Jpn. J. Appl. Phys. **1996**, 35, L1339. (b) Sano, T.; Nishio, Y.; Hamada, Y.; Takahashi, H.; Usuki, T.; Shibata, K. J. Mater. Chem. **2005**, 10, 157. (c) Yu, G.; Yin, S.; Liu, Y.; Shuai, Z.; Zhu, D. J. Am. Chem. Soc. **2003**, 125, 14816.
- (a) Haneline, M. R.; Tsunnodo, M.; Gabbai, F. P. J. Am. Chem. Soc. 2002, 124, 3737. (b) Atoub, N.; Mahmoudi, G.; Morsali, A. Inorg. Chem. Commun. 2007, 19, 166. (c) Mahmoudi, G.; Morsali, A.; Zhu, L.-G. Polyhedron 2007, 26, 2885.
- (a) Roberto, D.: Ugo, R.; Bruni, S.; Cariati, E.; Cariati, F.; Fantucci, P.; Invemizzi, I. Organometallics 2000, 19, 1775. (b) Roberto, D.; Ugo, R.; Tessore, F.; Lucenti, E.; Quici, S.; Vezza, S.; Fantucci, P.; Invemizzi, I.; Bruni, S.; Ledoux-Rak, I.; Zyss, J. Organometallics 2002, 21, 161. (c) Lucenti, E.: Cariati, E.; Dragonetti, C.: Manassero, L.: Tessore, F. Organometallics 2004, 23, 687. (d) Tessore, F.; Roberto, D.; Ugo, R.; Pizzotti, M.; Quici, S.; Cavazzini, M.; Bruni, S.; De Angelis, F. Inorg. Chem. 2005, 44, 8967.
- Liu, S. F.; Wu, Q.; Schmider, H. L.; Aziz, H.; Hu, N. X.; Popović, Z.; Wang, S. J. Am. Chem. Soc. 2000, 122, 3671.
- (a) Thomas, F.; Schulz, S.; Nieger, M. Angew. Chem. Int. Ed. 2005, 44, 5668. (b) Klappa, J. J.; Geers, S. A.; Schmidtke, S. J.; MacManus-Spencer, L. A.; McNeill, K. Dalton Trans. 2004, 6, 883.
- Kim, Y.-L.; Lee, Y.-S.; Seo, H.-J.; Lee, J.-Y.; Kang, S. K. Acta Cryst. 2007, E63, m2810.
- Durantaye, L. D. L.; McCormick, T.; Liu, X.-Y.; Wang, S. Dalton Trans. 2006, 48, 5675.
- Kim, Y.-L.; Lee, Y.-S.; Seo, H.-J.; Nam, K.-S.; Kang, S. K. Acta Cryst. 2008, E64, m358.
- Chen, X.; Zhou, Q.; Cheng, Y.; Geng, Y.; Ma, D; Xie, Z.; Wang, L. J. Luminescence 2007, 126, 81.
- 13. Lippert, E. Z. Naturforsch. 1955, 10a, 541.
- 14. Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; Mccoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* 1997, 97, 1515.
- He, A.; Ahong, C.; Huang, H.: Zhon, T.: Ma, Y.: Zhang, H. J. Luminescence 2008, 128, 1291.
- Lamansky, S.; Djurovich, P.; Marphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Ban, R.; Thompson, M. E. Inorg. Chem. 2001, 41, 1704.
- Bard, A. J.; Faulkner, L. R. In *Electrochemical Methods: Fundamentals and Application*, 2nd ed.; John Wiley & Sons Inc.: 2001; p. 54.
- Blanco, M. A.; López-Torres, E.; Mendiola, M. A.; Brunet, E.; Sevilla, M. T. *Tetrahedron* 2002, 58, 1525.