A blue photoluminescent [Zn(L)(CN)$_2$] (L = 2,2′-dipyridylamine) material with a supramolecular one-dimensional chain structure

Kin-Ying Ho, Wing-Yiu Yu, Kung-Kai Cheung and Chi-Ming Che*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

A novel blue luminescent [Zn(L)(CN)$_2$] complex (L = 2,2′-dipyridylamine) is synthesized and characterized by an X-ray diffraction study; the crystal packing in the Zn complex reveals that the molecules self-assemble by intermolecular hydrogen bonds [N–H···N≡C distance = 2.965(7) Å] and face-to-face π–π aromatic stacking interactions to form two-dimensional sheets.

Cyanometallates are useful motifs for the construction of supramolecular structures having novel photoelectronic properties; the superstructure formation is usually achieved through bridging linear covalent M–C≡N–M bonding interactions.[1] There have been relatively few attempts to harness terminal cyanide ligand as a binding site for hydrogen bonding in the synthesis of supramolecular assemblies. As part of our endeavour to explore the potential application of some blue luminescent metal complexes for molecular light-emitting diode device fabrications,[2] we are interested in the coordination chemistry of zinc(II) cyanides,[3] the luminescence properties of which have been little studied. Herein is decribed a blue luminescent cyanozinc(II) complex with 2,2′-dipyridylamine ligand L, [Zn(L)(CN)$_2$], and the solid state structure of which shows cooperative N–H···N≡C hydrogen bonding and π–π stacking interactions.

The zinc(II) complex was prepared by prolonged reflux of a methanolic suspension of Zn(CN)$_2$ with L.[†] Using hot methanol the product was isolated as pale yellow crystals suitable for an X-ray crystallographic study.[‡] Fig. 1 depicts a perspective view with atom numbering of the molecule. The Zn atom adopts a distorted tetrahedral coordination geometry and the measured Zn–N(1)/(3) distances are 2.037(4) and 2.046(4) Å, and the Zn–C(1)/(2) distances are found to be 1.987(6) and 2.007(6) Å. The observed Zn–N distances are comparable to the corresponding bond distances [2.148(9) and 2.082(9) Å] found for a related [Zn(L)(dien)](NO$_3$)$_2$ complex [dien = bis(2-aminoethyl)-amine].[4] The C(1)–Zn–C(2) bond angle is 108.3(2)°, whereas the N(1)–Zn–N(3) angle is 92.3(2)°.

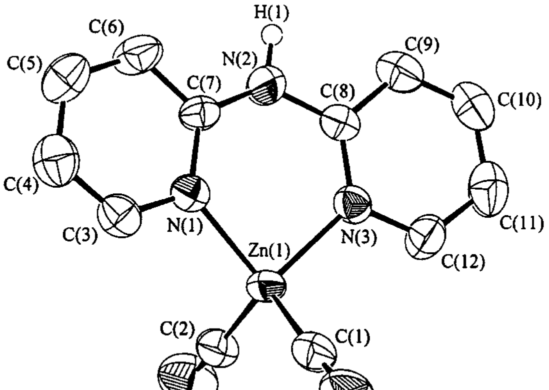

Fig. 1 Perspective view of [Zn(L)(CN)$_2$] [50% thermal ellipsoids except for H(1)] and atom-numbering scheme. Significant bond distances (Å) and angles (°): Zn(1)–N(1) 2.037(4); Zn(1)–N(3) 2.046(4); Zn(1)–C(1) 1.987(6); Zn(1)–C(2) 2.007(6); N(2)–H(1) 0.91(6). N(1)–Zn(1)–N(3) 92.3(2); N(1)–Zn(1)–C(1) 116.3(2), N(1)–Zn(1)–C(2) 108.4(2); N(3)–Zn(1)–C(1) 108.4(2); N(3)–Zn(1)–C(2) 110.0(2); C(1)–Zn(1)–C(2) 118.3(2).

As shown by the crystal packing (Fig. 2), the molecules are self-organized by extensive intermolecular hydrogen bonds between the amino and the cyano groups (N–H···N≡C) of the adjacent molecules, with obvious directionality and short intermolecular contact between successive nitrogen atoms [N···N distance = 2.965(7) Å]. The N(2)–H(1)···N(4) bond angle is 154(5)°, therefore a polymeric one-dimensional zigzag chain results. A related report by Cotton and co-workers[5] also revealed that the pseudo-tetrahedral [Co(L)$_2$] molecules stack together to form a one-dimensional ribbon with molecules linked through intermolecular hydrogen bonding. In the present [Zn(L)(CN)$_2$] complex face-to-face π–π stacking interactions between the aromatic rings of the 2,2′-dipyridylamine ligand are also evident, the interplanar separations are in the range 3.5–3.7 Å, and the glide-related complexes are linked in a head-to-head fashion to generate a supramolecular architecture of an infinite two-dimensional sheet. Inspection of the crystal packing shows that there are two kinds of two-dimensional sheets constituted by the same array of intermolecular forces but having the π–π stacking interactions aligning along different directions, hence a herringbone-type pattern is created.[6]

The spectroscopic and emission data of [Zn(L)(CN)$_2$] complex are listed in Table 1. In MeOH, the absorption spectrum of the complex is dominated by intraligand π–π* transitions at 255 and 315 nm. In solution, the complex displays a high energy emission with λ_{max} = 359 nm and τ = 10 ns at 298 K. Because there is no significant shift in emission energy for the related [Zn(L)X$_2$] (X = CN, OAc, Cl) complexes,[†] the emission is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature. We tentatively assign it to the intraligand $^1(\pi$–$\pi^*)$ fluoresence since a similar emission with λ_{max} at 357 nm is also observed for the free ligand. Interestingly, in both solid state and in 77 K MeOH–EtOH glassy solution, the corresponding intraligand $^3(\pi$–$\pi^*)$

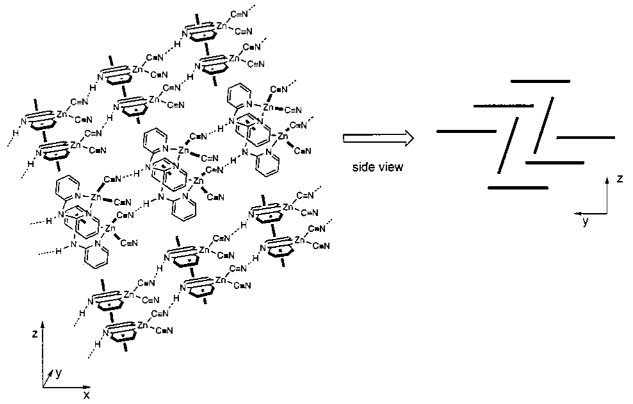

Fig. 2 Herringbone-type crystal packing pattern of [Zn(L)(CN)$_2$] molecules. The molecules are self-assembled to form extended 2-D sheets by cooperative π–π stacking interactions and extensive intermolecular hydrogen (N–H···N≡C) bonds.

Table 1 Photophysical data for $[Zn(L)(CN)_2]$ and derivatives

Complex	UV–VIS λ/nm (ε/dm^3 mol^{-1} cm^{-1})^a	Emission λ/nm 298 K^b	77 K^c	Solid state^d
$[Zn(L)(CN)_2]$	257 (18000), 316 (16000)	359	351, 392	363, 418
$[Zn(L)(OAc)_2]$	257 (20000), 315 (18000)	359	349, 389	378
$[Zn(L)Cl_2]$	255 (18000), 315 (17000)	360	348, 390	378

^{a} In MeOH at 298 K. ^{b} In degassed MeOH. ^{c} In MeOH–EtOH (1 : 2). ^{d} At 298 K.

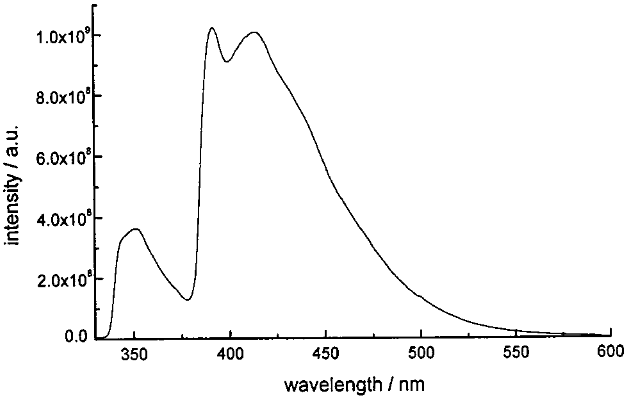

Fig. 3 Emission spectrum of $[Zn(L)(CN)_2]$ (excited at 315 nm) in MeOH–EtOH (1 : 2) glassy solution at 77 K.

phosphorescence has also been observed. As shown in Fig. 3, the lower energy $^3(\pi–\pi^*)$ emission at 392 nm (lifetime = 0.33 μs) shows a well resolved vibronic structure with a vibrational spacing of *ca.* 1350 cm^{-1} that is assigned to the skeletal stretching of the ligand.

The $[Zn(L)(CN)_2]$ complex shows an extended two-dimensional structure through cooperative hydrogen bonding and π–π stacking interactions. Its polymeric structure and the blue photoluminescence highlight the potential application of the zinc(II) cyanide complex as an advanced material for blue-light emitting diode devices.

We acknowledge the support from The University of Hong Kong and The Hong Kong Research Grants Council.

Notes and References

† *Preparation* of $[Zn(L)(CN)_2]$. A methanolic solution (20 cm^3) of L (0.17 g, 1 mmol) was added to a refluxing suspension of $Zn(CN)_2$ (0.12 g, 1 mmol) in MeOH (30 cm^3). The mixture was refluxed overnight. After cooling to room temperature, the white solid was collected by filtration. The product complex was extracted from the white solid into boiling methanol, and pale yellow crystals were obtained on cooling of the hot methanolic extract (overall yield: 60%). FT-Raman: 2164, 2153, 1619, 1587 and 1436 cm^{-1}. ^{1}H NMR (270 MHz, CD_3OD, TMS): δ 10.11 (s, 1H), 8.20 (d, 2H, ^3J = 4.3 Hz), 781 (t, 2H, ^3J = 7.3 Hz), 7.56 (d, 2H, ^3J = 7.2 Hz), 7.02 (t, 2H, ^3J = 6.0). FAB-MS: *m*/*z* 289 [M]$^+$, 261 [M − CN]$^+$. Anal. Calc. for $C_{12}H_9N_5Zn$ (M_r = 288.62): C, 49.94; H, 3.14; N, 24.27. Found: C, 49.99; H, 3.02; N, 24.41%.

Preparation of $[Zn(L)(OAc)_2]$. A methanolic solution (20 cm^3) of L (0.17 g, 1 mmol) was added to a refluxing solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.22 g, 1 mmol) in MeOH (30 cm^3). The mixture was refluxed overnight. After cooling to room temperature, the solvent was removed by rotary evaporation, and the white residue was recrystallized by slow diffusion of diethyl ether into methanolic solution to afford colorless crystals (overall yield: 85%). ^{1}H NMR (270 MHz, CD_3OD, TMS): δ 8.38 (dd, 2H, ^4J = 1.2 Hz, ^3J = 5.6 Hz), 7.93 (td, 2H, ^4J = 1.9 Hz, ^3J = 7.9 Hz), 7.20 (d, 2H, ^3J = 8.6 Hz), 7.16 (td, 2H, ^3J = 6.5, ^4J = 1.0 Hz). FAB-MS: *m*/*z*: 294 [M - OAc]$^+$. Anal. Calc. for $C_{14}H_{15}N_3O_4Zn$ (M_r = 354.67): C, 47.41; H, 4.26; N, 11.85. Found: C, 47.25; H, 4.21; N, 11.92%.

Preparation of $[Zn(L)Cl_2]$. A similar procedure as for $[Zn(L)(OAc)_2]$ was employed, except that hot DMF was used for recrystallization (overall yield: 80%). ^{1}H NMR (270 MHz, CD_3OD, TMS): δ 8.20 (d, 2H, ^3J = 2.6 Hz), 7.80 (m, 2H), 7.58 (d, 2H, ^3J = 8.4 Hz), 7.01 (t, 2H, ^3J = 6.3 Hz). FAB-MS: *m*/*z* = 270 [M − Cl]$^+$. Anal. Calc. for $C_{10}H_9Cl_2N_3Zn$ (M_r = 307.49): C, 39.06; H, 2.95; N, 13.67. Found: C, 38.93; H, 2.99; N, 13.75%.

‡ *Crystal data* for $[Zn(L)(CN)_2]$: $M_r = 288.62$, monoclinic, space group *Cc* (no. 9), $a = 16.305(1)$, $b = 6.445(2)$, $c = 13.166(3)$ Å, $\beta = 115.24(1)°$, $U = 1251.5(5)$ Å^3, $Z = 4$, $D_c = 1.532$ g cm^{-3}, μ(Mo-Kα) = 19.51 cm^{-1}, $F(000) = 584$, $T = 301$ K, 1084 unique reflections ($2\theta < 48°$, $R_{int} = 0.012$) were measured and 931 with $I > 3\sigma(I)$ were used in the refinement. $R = 0.024$, $R_w = 0.030$ with a goodness-of-fit of 1.62. CCDC 182/974.

1 (*a*) K. R. Dunbar and R. A. Heintz, in *Progress in Inorganic Chemistry*, ed. K. D. Karlin, John Wiley, New York, 1997, vol. 45, p. 283.
2 (*a*) C.-F. Lee, K.-F. Chin, S.-M. Peng and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 467; (*b*) Y. Ma, H.-Y Chao, Y. Wu, W.-Y. Yu and C.-M. Che, *Chem. Commun.*, 1998, in press.
3 (*a*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546 and references therein; (*b*) M. Uchiyama, Y. Kondo, T. Miura and T. Sakamoto, *J. Am. Chem. Soc.*, 1997, **119**, 12372.
4 N. Ray and B. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1980, 1150.
5 F. A. Cotton, L. M. Daniels, G. T. Jordan IV and C. A. Murillo, *Chem. Commun.*, 1997, 1673.
6 J. J. Wolff, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2195.

Received in Cambridge, UK, 27th July 1998; 8/05814H