

Synthesis, structures and luminescent properties of [ZnCl₂(2,6-bis{1-(phenylimino)ethyl}pyridine)]

Xuefu Li, Dongsheng Zhu, Wei Gao, Yuetao Zhang and Ying Mu*

School of Chemistry, Jilin University, Chang Chun 130012, People's Republic of China

The complex 2, 6-Bis[1-(phenylimino)ethyl pyridine ZnCl₂ (**3**) was synthesised via the reaction of ZnCl₂ with the 2,6-bis[1-(phenylimino)ethyl]pyridine (**L**₃) in CH₂Cl₂ and its structure determined by single-crystal X-ray diffraction. The geometry of **3** can be best described as distorted trigonal bipyramidal. **3** has blue luminescence at room temperature in solution and the solid state which is assumed to be from a $\pi^* \rightarrow \pi$ transition centred on the ligand. The Zn(II) centre plays a key role in enhancing fluorescent emission of the ligand.

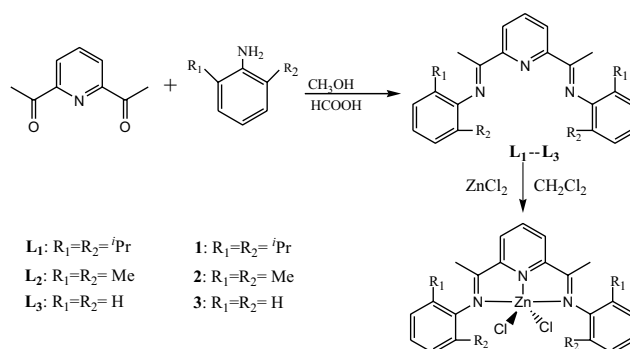
Keywords: bis(imino)pyridyl, Zn, crystal structure, blue luminescence

Luminescent organic and coordination compounds have been an active research area for decades due to their various potential applications in molecular optical or electronic devices and chemical sensors.¹ One of the most important considerations in light-emitting devices (LEDs) is the design and modification of the ligands subunit.² It has been found that the size of the π -conjugated system of the ligands and the electronic effect of substituents on the ligands are vital factors for tuning its luminescent properties.³ In particular, π -conjugated organic compounds with aromatic nitrogen heterocycles, which can be receptors for metal ions, have attracted much attention for their good electrochemical, photophysical and photochemical features.⁴ Recently, we have treated a substituent aniline with 2,6-diacetylpyridine in order to produce a large π -conjugated system and two bis(imino)pyridylzinc complexes [ZnCl₂(2,6-bis{1-(2,6-diisopropylphenylimino)ethyl}pyridine)] (**1**) and [ZnCl₂(2,6-bis{1-(2,6-dimethylphenylimino)ethyl}pyridine)] (**2**) were synthesised.⁵ It was found that **1** and **2** have blue luminescence at room temperature in solution and the solid state. In order to investigate the electronic effect of substituents of this type of complex, we herein report one new Zn(II) complex, 2,6-bis[1-(phenylimino)ethyl]pyridylzinc dichloride (**3**) and investigate the electronic effect of substituents at the aryl-ring of the bis(imino)pyridyl ligand on the luminescent properties of complexes (**1**–**3**).

Results and discussion

Synthesis and characterisation

2,6-bis[1-(phenylimino)ethyl]pyridine (**L**₃) was synthesised according to a modified published procedure in good yield by condensation of 2, 6-diacetylpyridine with aniline in refluxing absolute methanol in the presence of a catalytic amount of formic acid (Scheme 1).⁶ Zinc complex **3** was synthesised by reactions of the ligand (**L**₃) with ZnCl₂ in CH₂Cl₂ at room temperature (Scheme 1). Complex **3** was obtained as yellowish crystals in good yield.



Scheme 1

All compounds were characterised by ¹H NMR, UV/Vis, IR and elemental analyses. Complex **3** was also studied by single-crystal X-ray diffraction.

Description of structures

The molecular structure of complex **3** was determined and the ORTEP drawing of the molecular structure is shown in Fig. 1. Selected bond lengths and angles are summarised in Table 1. There are two independent molecules (**3A** and **3B**) with minor structural differences and two CH₂Cl₂ molecules in the unit cell of **3**. Selected bond lengths and angles for **3A** will be used in subsequent discussions. The general structure features of **3** are comparable to those previously reported for **1**, **2**. All molecules adopt C_s-symmetry with distorted trigonal bipyramidal geometry for the metal centre, with the pyridyl nitrogen atom and two chlorine atoms forming the equatorial plane and the two N (imino) atoms in the axial positions. The equatorial angles range of **3** between 98.40(6) and 142.12(6) is similar to the ranges for **1** and **2**. The N(1)–Zn(1)–N(3) angles of **3** (146.8(4)°), **1** (139.88(8)°) and **2** (147.76(12)°) are bigger than 130°, which exhibits the

Table 1 Selected bond lengths and angles in complex **3A**

Complex 3A			
Zn(1)–N(1)	2.254(10)	Zn(1)–Cl(2)	2.214(4)
Zn(1)–N(2)	2.067(10)	N(1)–C(1)	1.274(13)
Zn(1)–N(3)	2.283(10)	N(3)–C(7)	1.270(14)
Zn(1)–Cl(1)	2.256(10)		
N(2)–Zn(1)–N(1)	73.8(4)	N(2)–Zn(1)–Cl(1)	118.1(3)
N(1)–Zn(1)–Cl(1)	97.5(3)	N(2)–Zn(1)–N(3)	73.1(4)
N(1)–Zn(1)–N(3)	146.9(4)	Cl(1)–Zn(1)–N(3)	96.5(3)
N(2)–Zn(1)–Cl(2)	124.9(3)	N(1)–Zn(1)–Cl(2)	101.9(3)
Cl(1)–Zn(1)–Cl(2)	116.97(16)	N(3)–Zn(1)–Cl(2)	98.2(3)

* Correspondent. E-mail: gw@jlu.edu.cn

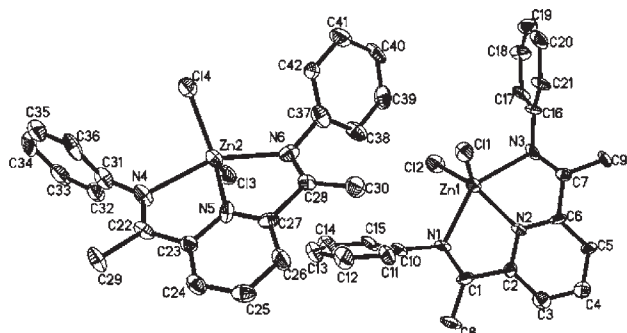


Fig. 1 Molecular structure of **3**. Solvent molecules and hydrogen atoms were omitted for clarity.

distorted extent of the frame. The dihedral angles between the phenyl rings and the plane formed by three coordinated nitrogen atoms are $[76.47(47)^\circ$ and $88.59(48)^\circ]$. The angles are $[80.38(11)^\circ$ and $[81.22(08)^\circ]$ in **1** and $[81.23(16)^\circ$ and $88.85(14)^\circ]$ in **2**, respectively. The Zn atom in **3** lies 0.0461 \AA out of the plane of three coordinated nitrogen atoms, which is smaller than those for complexes **1** (0.056 \AA) and **2** (0.079 \AA). The mean deviation of the zinc atom from the equatorial plane is 0.0351 \AA in **3**, 0.013 \AA in **1**, and 0.011 \AA in **2**. The two imino C=N bonds with C=N bond lengths of $1.273(13)$ and $1.271(14) \text{ \AA}$ in **3**, $1.272(3)$ and $1.278(3) \text{ \AA}$ in **1**, and $1.277(5)$ and $1.274(5) \text{ \AA}$ in **2** have typical double-bond character.

Luminescence properties

The three complexes show two main absorption bands, which are similar to ligands L_1 – L_3 in the UV region, as shown in Figs 2 and 3. The electronic absorption spectra of the complexes show low-energy absorption bands at about 358 – 365 nm (329 – 340 nm for ligands L_1 – L_3), and higher energy absorption bands at about 288 – 301 nm (281 – 291 nm for ligands L_1 – L_3), attributed to ligand-centred π – π^* transitions. The electronic absorption spectra of the complexes are red-shifted relative to the ligands due to perturbation of the ligand π – π^* transition of the bis(iminoalkyl)pyridine unit by the metal atom. The energy trends of this band for the series **1**–**3** and L_1 – L_3 are found to follow the order $3 > 1 > 2$ and $L_3 > L_1 > L_2$. Complexes **1**–**3** have broad fluorescent emission

Table 2 Crystal data and structure refinement for complex **3**

Data	3
Formula	$C_{22}H_{21}Cl_4N_3Zn_1$
Fw	534.59
Temperature/K	293(2)
crystal system	Triclinic
space group	$P-1$
$a/\text{\AA}$	13.316(2)
$b/\text{\AA}$	14.827(3)
$c/\text{\AA}$	13.538(2)
$\beta/^\circ$	106.975(3)
Volume/ \AA^3	2412(2)
Z	4 ^a
$D_{\text{calcd}}/\text{g m}^{-3}$	1.472
$F(000)$	1088
θ range for data collection	1.89° to 25.01°
Limiting indices	$-10 \leq h \leq 8$, $-12 \leq k \leq 15$, $-15 \leq l \leq 23$
Data/restraints/parameters	6414/6/545
Goodness-of-fit on F^2	0.728
Final R indices $[I > 2\sigma(I)] R_1^b$	0.0693
R indices (all data) wR_2^c	0.1784
Largest diff. peak and hole/ $e.\text{\AA}^{-3}$	0.641 and -0.617

^aThere are two crystallographically independent molecules in the asymmetric unit.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}$

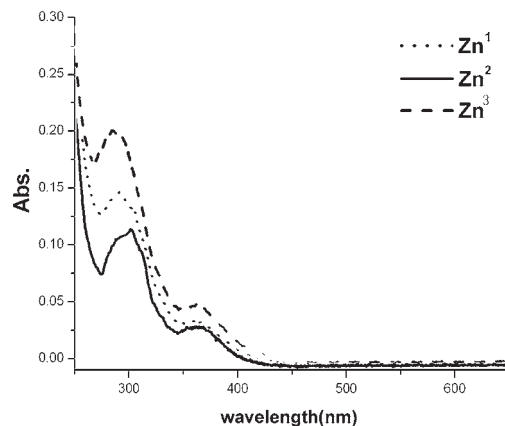


Fig. 2 UV spectrum of **1**, **2** and **3**.

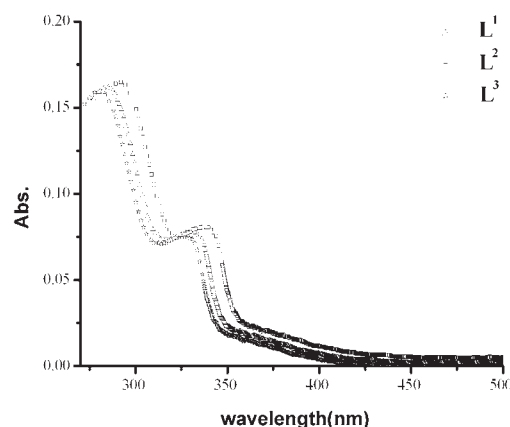


Fig. 3 UV spectrum of L_1 , L_2 and L_3 .

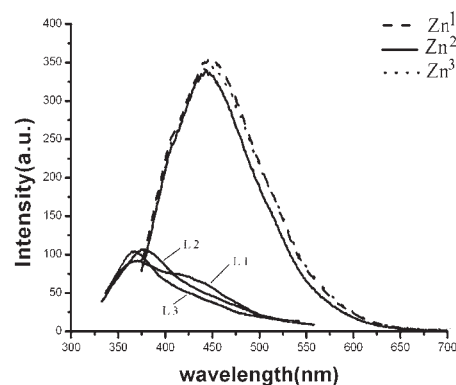


Fig. 4 Fluorescent emission spectrum of **1**, **2** and **3**.

bands in degassed CH_2Cl_2 solution at room temperature, with maxima at 445 , 450 , and 440 nm for **1**–**3**, respectively ($\lambda_{\text{max}} = 375$, 381 , and 368 nm for L_1 – L_3 ; Figure 4). Similar to the electronic absorption data, the emission energies are found to depend on the bis(iminoalkyl)pyridine ligands. For complexes **1**–**3** and ligands L_1 – L_3 , emission-energy trends in the order $3 > 1 > 2$ and $L_3 > L_1 > L_2$ are observed, again in line with the electron-donating ability of the alkyl group. The Zn(II) centres in complexes **1**–**3** play a key role in enhancing the fluorescent emission of the ligands. The chelation of the ligands to the metal centre also contributes to the enhancement of the fluorescent emission by increasing the rigidity of the ligands, thus reducing the loss of energy by thermal vibrational decay. However, in the solid state at room temperature complexes **1**–**3** exhibit a bright, greenish-blue emission band with

maxima at 484, 486, and 483 nm, respectively ($\lambda_{\text{max}} = 475, 480,$ and 471 nm for L_1-L_3); these values are redshifted by about 40 nm (100 nm for L_1-L_3) from the emission in solution. This dramatic redshift of the emission energy for complexes **1-3** and ligands L_1-L_3 from solution to the solid state is probably caused by intermolecular interactions in the solid state that effectively decrease the energy gap.

Conclusion

Complex **3** has been synthesised and characterised. Complexes **1-3** and ligands L_1-L_3 have fluorescent emission at 368–450 nm in dichloromethane solution at room temperature. Complexes **1-3** and ligand L_1-L_3 have broad fluorescent emission bands in CH_2Cl_2 solution at room temperature, with $\lambda_{\text{max}} = 445, 450,$ and 440 nm for **1-3**, and 375, 381, and 368 nm for L_1-L_3 respectively. Their luminescent properties show that they are a new class of luminescent metal compounds with potential applications in LEDs.

Experimental

General comments

Reactions with organometallic reagents were carried out under a nitrogen atmosphere (ultrahigh purity) using standard Schlenk techniques.⁷ Solvents were dried and distilled prior to use.⁸ ^1H NMR spectra were recorded on a Varian Mercury 300 MHz or Bruker ACF 500 MHz spectrometer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 240c element analyser. UV-vis spectra were obtained on a Perkin-Elmer Lambda 20 spectrometer. Luminescence spectra were measured on a Perkin-Elmer LS55 Luminescence spectrometer at room temperature. 2-methylaniline was purchased from Aldrich Chemical Co. and used as received. 2,6-Diacetylpyridine was prepared according to literature procedure.⁹

2,6-bis[1-(phenylimino)ethyl]pyridine (L_3): Aniline (2.8 ml, 31.0 mmol) was added to a solution of 2,6-diacetylpyridine (1.70 g, 10.4 mmol) in absolute methanol (30 ml). After the addition of several drops of formic acid, the reaction mixture was refluxed for 8 h and then allowed to cool down to room temperature. The crude product precipitated as a yellow powder. Pure L_3 was obtained in 88 % yield (2.87 g) upon recrystallisation from methanol. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.36$ (d, $J = 7.8$ Hz, 2 H, Py-*Hm*), 7.89 (t, $J = 7.8$ Hz, 1 H, Py-*Hp*), 7.42–6.85 (m, 10 H, Ar-*H*), 2.42 (s, 6 H, N = *CMe*) ppm. IR (KBr): 3059 (w), 2919 (w), 2860 (w), 1638 (vs), 1594 (m), 1574 (m), 1482 (s), 1445 (m), 1417 (w), 1361 (s), 1319 (m), 1294 (w), 1255 (w), 1220 (s), 1173 (m), 1150 (w), 1118 (m), 1091 (m), 1076 (m), 1027 (m), 992 (w), 969 (w), 912 (w), 874 (w), 823 (s), 808 (m), 774 (s), 762 (m), 743 (m), 707 (s), 697 (m), 658 (w), 645 (w), 551 (w), 520 (m), 468 (w), 443 (w) cm^{-1} . $\text{C}_{21}\text{H}_{19}\text{N}_3$ (313.4): calcd. C 80.5, H 6.1, N 13.4; found C 80.3, H 6.0, N 13.3.

2,6-bis[1-(phenylimino)ethyl]pyridineZnCl₂ (3**):** A mixture of L_3 (125.4 mg, 0.4 mmol) and ZnCl_2 (54.5 mg, 0.4 mmol) in CH_2Cl_2 (35 ml) was stirred under dinitrogen at room temperature for 12 h. Evaporation of the solvent gave the crude product as yellow powder. Pure product **3** was obtained in 83 % yield (149.3 mg) by recrystallisation from $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (2: 1 by volume). ^1H NMR (300 MHz, CD_3CN): $\delta = 8.50$ (quint, $J = 7.2$ Hz, 3 H, Py-*H*), 7.52–7.17 (m, 10 H, Ar-*H*), 2.52 (s, 6 H, N = *CMe*) ppm. ^{13}C NMR (CD_3CN , 1H gated decoupled): $\delta = 166.30$ (N = C), 148.41 (Py-*Co*), 147.39 (Ar-*Ci*), 143.44 (Ar-*Co*), 129.27 (Ar-*Cp*), 128.09 (Py-*Cp*), 126.37 (Py-*Co*), 121.66 (Ar-*Co*), 17.46 (N = *CMe*) ppm. IR (KBr): 3089 (w), 3029 (w), 2960 (w), 2915 (w), 2247 (w), 1631 (s), 1591 (s), 1487 (s), br 1450 (m), 1371 (s), 1309 (w), 1284 (w), 1252 (s), 1227 (s), 1185 (w), 1148 (w), 1103 (w), 1071 (w), 1019 (m), 981 (w),

909 (w), 859 (w), 820 (s), 777 (s), 758 (m), 743 (m), 725 (m) 697 (s), 674 (w), 654 (w), 576 (w), 552 (w), 533 (m), 468 (w), 407 (w) cm^{-1} . $\text{C}_{21}\text{H}_{19}\text{ZnCl}_2\text{N}_3$ (558.1): calcd. C 56.1, H 4.3, N 9.3; found C 56.2, H 4.5, N 9.3.

X-ray crystallography

The single-crystal X-ray diffraction data for complex **3** were collected on a Siemens SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å), operating at 293±2 K. The structures were solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL 5.1 software package.¹⁰ Crystallographic data are given in Table 2. The CIF file of **3** has been deposited to the CCDC with the CCDC No. 279468.

Received 8 August 2005; accepted 10 November 2005
paper 05/3417

References

- (a) T. Skotheim, R. Elsenbaumer and J. Reynolds, (eds), *Handbook of Conducting Polymers*, 2nd edn; Marcel Dekker: New York, 1998; (b) H. Kies, (ed), *Conjugated Conducting Polymers*, Springer Series in Solid-State Physics, Vol. 102; Springer: Berlin, 1992; (c) J.L. Bredas and R. Sylbey, (eds); *Conjugated polymers*; Kluwer: Dordrecht, The Netherlands, 1991; (d) A.O. Patil, A.J. Heeger and F. Wudl, *Chem. Rev.*, 1988, **88**, 183; (e) J.S. Miller, *Adv. Mater.*, 1993, **5**, 671; (f) T. Yamamoto, *J. Synth. Org. Chem. Jpn.*, 1995, **53**, 999; (g) H. Bassler, and L.J. Rothberg, *Chem. Phys.*, 1998, **227**, 1; (h) A. Kraft, A.C. Grimsdale and A.B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402; (i) A.D. Schlüter and G. Wegner, *Acta Polym.*, 1993, **44**, 59; (j) *Chemosensors of Ion and Molecule Recognition*; J.-P. Desvergne, A.W. Czarnik, (eds); NATO ASI Series; Kluwer Academic: Dordrecht, 1997; Vol. C492; (k) A.W. Czarnik, *Chem. Biol.*, 1995, **2**, 423; (l) J.M. Tour, *Chem. Rev.*, 1996, **96**, 537; (m) L.R. Jones, J.S. Schumm and J.M. Tour, *J. Org. Chem.*, 1997, **62**, 1388; (n) J.S. Moore, *Acc. Chem. Res.*, 1997, **30**, 402; (o) M. Moroni, J. LeMoigne and S. Luzzati, *Macromolecules*, 1994, **27**, 562; (p) U. Ziener and A. Godt, *J. Org. Chem.*, 1997, **62**, 6137; (q) H. Kukula, S. Veit and A. Godt, *Eur. J. Org. Chem.*, 1999, 277; (r) A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher and T.E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
- (a) R.D. McCullough, *Adv. Mater.*, 1998, **10**, 93; (b) S. Yamaguchi, T. Shirasaka and K. Tamao, *Org. Lett.*, 2000, **24**, 4129; (c) T. Noda, H. Ogawa, N. Noma and Y. Shirota, *Adv. Mater.*, 1997, **9**, 720; (d) M. Berggren, O. Inganäs, G. Gustafsson, J. Rasmussen, M.R. Andersson, T. Hjertberg and O. Wennerstrom, *Nature*, 1994, **372**, 444; (e) Y. Ohmori, M. Uchida, K. Kuro and K. Yoshino, *Jpn. J. Appl. Phys.*, 1991, **30**, L1938.
- (a) L.V. Sazanovich, C. Kirmaier, E. Hindin, L. Yu, D.F. Bocian, J.S. Lindsey and D. Holten, *J. Am. Chem. Soc.*, 2004, **126**, 2664; (b) Y. Kang, C. Seward, D. Song and S. Wang, *Inorg. Chem.*, 2003, **42**, 2789; (c) V.W.W. Yam, Y.L. Pui and K.K. Cheung, *New J. Chem.*, 1999, **23**, 1163.
- (a) G.A. Crosby, R.J. Watts and D.H.W. Carstens, *Science*, 1970, **170**, 1195; (b) V. Balzani, F. Bolletta, M.T. Gandolfi and M. Maestri, *Top. Curr. Chem.*, 1978, **75**, 1; (c) M.K. De Armond and C.M. Carlin, *Coord. Chem. Rev.*, 1981, **36**, 325; (d) T.J. Meyer, *Pure Appl. Chem.*, 1986, **58**, 1193; (e) A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85; (f) K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, U.K., 1992.
- Fan Rui-Qing, Zhu Dong-Sheng, Mu Ying, Li Guang-Hua, Yang Yu-Lin, Su Qing, and Feng Shou-Hua *Eur. J. Inorg. Chem.*, 2004, 4891.
- (a) E.C. Alyea and P.H. Merrell, *Synth. React. Inorg. Met. Org. Chem.*, 1974, **4**, 535; (b) B.L. Small, M. Brookhart and A.M.A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049–4050; (c) G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White and D.J. Williams, *Chem. Commun.*, 1998, 849.
- D.F. Shriver, *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.
- D.D. Perrin, W.L.F. Armarego and D.R. Perrin, *The Purification of Laboratory Chemicals*, Pergamon: New York, 1980.
- J.Z. Zhong and F. Wang, *Acta Acad. Med. Jiangxi*, 1999, **39**, 93.
- SHELXTL NT Crystal Structure Analysis Package, version 5.10, Bruker AXS, Analytical X-ray System, Madison, WI, 1999.