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Zinc(II) mediated synthesis of an N-substituted 2-(2-pyridyl)imidazole from a 1,2-diketone and 2-(aminomethyl)pyridine and its ligational behaviour

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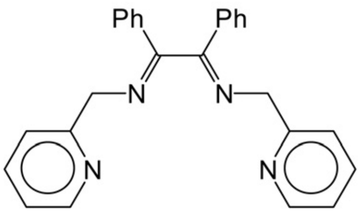
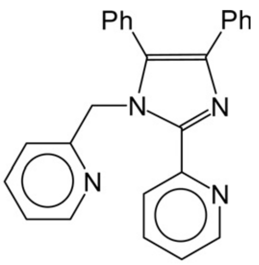
Reaction of anhydrous $ZnCl_2$ with the 1:2 condensate (L) of benzil and 2-(aminomethyl)pyridine in methanol gives monomeric $ZnL'Cl_2$ (**1**) where L′ is 2-[(4,5-diphenyl-2-pyridin-2-yl-1*H*-imidazol-1-yl)-methyl]pyridine. In the X-ray crystal structure, **1** is found to contain tetrahedral zinc with an N_2Cl_2 coordination sphere and the N-substituent methylpyridine fragment hanging as a free arm. A tentative mechanism is proposed for the zinc mediated conversion of L → L′. Demetallation of **1** by the action of aqueous NaOH yields L′ in the free state. When L′ is reacted with $Zn(ClO_4)_2{\cdot}6H_2O$ in a 1:2 molar proportion, $[Zn(L')_2]_n(ClO_4)_{2n}{\cdot}(H_2O)_{n/2}{\cdot}(CH_2Cl_2)_{n/2}$ (**2**) is obtained. The zinc atom in **2**, as revealed by X-ray crystallography, has a trigonal bipyramidal N_5 coordination sphere. There are two independent ligands in the asymmetric unit of **2**. One of them bonds only to one zinc atom in a bidentate mode with the N-substituent methylpyridine hanging free while the other ligand binds to two different zinc atoms in a tridentate fashion, employing the N-substituent methylpyridine nitrogen atom to form the polymeric one-dimensional chain cation.

Introduction

2-(2-Pyridyl)imidazole can be considered as a hybrid of 2,2′-bipyridine and 2,2′-biimidazole, which are versatile N-donor ligands in transition metal chemistry.[1] Its chemistry, which has not been explored thoroughly,[2] is our concern here. A convenient route for its synthesis is to react glyoxal, ammonia and 2-formylpyridine in aqueous ethanol at low temperature.[3] While an excess of ammonia is needed in this procedure, glyoxal and 2-formylpyridine are used in a 1:1.2 molar proportion. In our attempt to synthesise a simple zinc complex of the ligand L, the 1:2 condensate of benzil and 2-(aminomethyl)pyridine, we have obtained a zinc complex of L′, which is an N-substituted 2-(2-pyridyl)imidazole. These results, together with the isolation of L′ in the free state and its use as a novel tridentate N-donor ligand, are reported here.



(L)



(L′)

Results and discussion

The ligand L is prepared by refluxing benzil and 2-(aminomethyl)pyridine in a 1:2 molar proportion in anhydrous methanol. It is obtained as a reddish yellow gum. As isolated, it is not analytically pure. All our attempts to purify it by chromatography have so far failed. Such problems with Schiff bases are not new.[4] However, by reacting it with anhydrous zinc chloride in methanol at room temperature, we obtain red crystals of **1** in good yield. From X-ray crystallography, **1** is found to be $ZnL'Cl_2$ in which the chloride ions are coordinated to the metal and the ligand moiety L′ is bound to the metal in a bidentate mode (Fig. 1). The geometry about the zinc ion is distorted tetrahedral with angles ranging from 79.82(1)° to 118.2(1)°. With the exception of the angle formed by the bidentate bite of the organic ligand the other angles fall in a narrow range, 114° ± 4°. The two Zn–Cl bonds are more or less indistinguishable. The $Zn–N_{pyridyl}$ bond, 2.069(4) Å, is significantly longer than the bond to the other metallated nitrogen atom, 2.028(3) Å. The two metallated rings are essentially coplanar, with an angle between mean planes of 5.3°, while the phenyl substituents on the imidazole ring form angles of 37.3° and 62.7° with that five-membered ring.

A tentative mechanism for the zinc mediated transformation of L to L′ is suggested in Scheme 1. In the first step, L is proposed to bind the metal in a bidentate fashion. In the last step, an aerial oxidation is implicated. When the reaction between anhydrous zinc chloride and L is carried out under an N_2 atmosphere, $ZnL'Cl_2$ is not formed; instead, a pink amorphous zinc complex is obtained, which we have not yet been able to characterise. In the observed reaction of $ZnCl_2$ with L, Zn^{2+} does not act as a simple Lewis acid. Binding of L to zinc seems to be a prerequisite for the transformation L → L′, as simple proton (reacted with L in the form of perchloric acid) is found to be ineffective in this regard.

Demetallation of **1** by the action of aqueous NaOH affords L′ in the free state. In contrast to L, L′ is obtained as a pure

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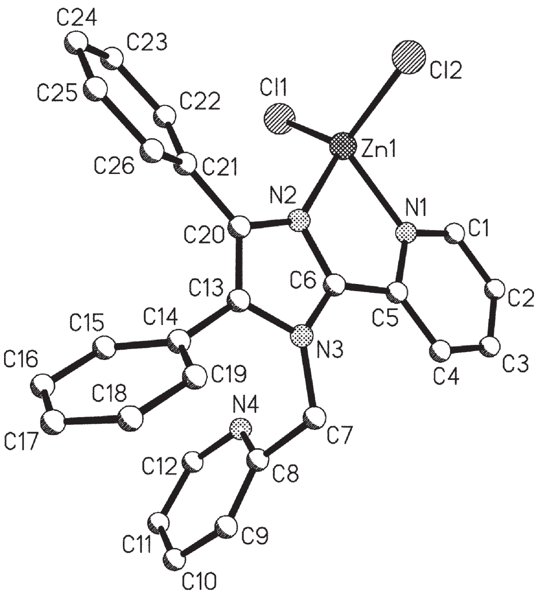
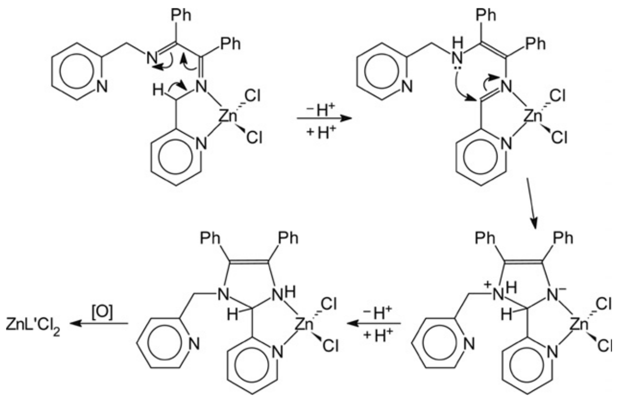


Fig. 1 A view of the structure of $ZnL'Cl_2$ (**1**). Selected bond distances (Å) and angles (°): Zn1–N1 2.069(4), Zn1–N2 2.028(3), Zn1–Cl1 2.205(1), Zn1–Cl2 2.208(1), N2–Zn1–N1 79.8(1), N2–Zn1–Cl1 116.4(1), N1–Zn1–Cl1 111.9(1), N2–Zn1–Cl2 114.1(1), N1–Zn1–Cl2 109.9(1).

solid. Complex **1** can be easily regenerated by reacting anhydrous zinc chloride with free L′ in equimolar amounts in methanol.

Reaction of L′ with $ZnClO_4{\cdot}6H_2O$ in a 2:1 molar proportion in tetrahydrofuran and subsequent recrystallisation of the product from a mixture of dichloromethane and petroleum ether yields $[Zn(L')_2](ClO_4)_2{\cdot}\frac{1}{2}H_2O{\cdot}\frac{1}{2}CH_2Cl_2$ (**2**). Its structure, as revealed by X-ray crystallography, consists of an infinite one-dimensional polymeric cation $[Zn(L')_2]_n^{2n+}$ (Fig. 2) and free perchlorate anions and solvent molecules. The polymeric chain extends along the *b* axis. The environment of a single zinc atom is shown in Fig. 3. The metal atom is bonded to five nitrogen atoms from three different ligands and has a trigonal bipyramidal environment. The coordination sphere contains bonds to two nitrogen atoms from each of two ligands forming five-membered chelate rings with the metal, thus N(21) at 2.055(12) Å and N(11) at 2.130(12) Å form a chelating ring as does N(91) $(0.5-x,\ 0.5+y,\ 0.25-z)$ at 2.066(12) Å and N(101) $(0.5-x,\ 0.5+y,\ 0.25-z)$ at 2.119(11) Å. N(11) and N(101), which are pyridine nitrogen atoms, are the axial atoms in the coordination sphere and form the longer bonds to the metal atom. The coordination sphere is completed by N(81), a pyridine nitrogen from a third ligand. There are two independent ligands in the asymmetric unit, one bonding to only one zinc atom while the other bonds to two different zinc atoms, thus forming the polymeric chain shown in Fig. 2.



Scheme 1 Proposed mechanism for the zinc mediated conversion of L to L′ in the coordinated state. Only the active H atoms are shown.

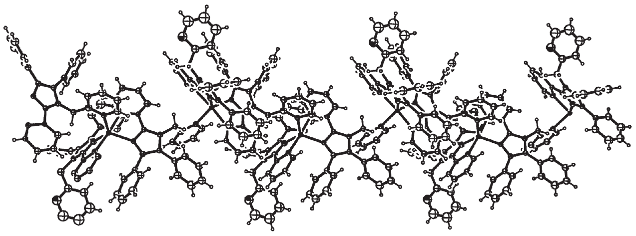


Fig. 2 The structure of the one-dimensional polymeric cation in **2** with ellipsoids at 25% probability.

Concluding remarks

Here we report an easy procedure for synthesising an N-substituted 2-(2-pyridyl)imidazole. No N-substituted 2-(2-pyridyl)-imidazole with a pendant donor atom has been reported earlier. The zinc assisted aerial oxidation in the last step of Scheme 1 is reminiscent of the activity of liver alcohol dehydrogenase (LADH), which is a zinc containing metalloenzyme. The zinc(II) center in LADH binds alcohol in the catalytic cycle of the enzyme, facilitating the oxidation of alcohol by NAD^+ (oxidised form of nicotinamide adenine dinucleotide).[5,6]

Our work shows that L′ can behave as a bidentate as well as a tridentate N-donor ligand. In the bidentate mode, the N-substituent methylpyridine remains free. When this pendant pyridine N takes part in binding, L′ becomes tridentate. In the tridentate mode, it is capable of generating coordination polymers, which are of much current interest because of their possible applications as functional materials.

Experimental

Microanalyses were performed with the use of a Perkin–Elmer 2400II elemental analyser. FTIR spectra (KBr) were recorded on a Nicolet Magna-IR (Series II) spectrophotometer, UV-VIS spectra on a Shimadzu UV-160A spectrophotometer and ^{1}H NMR spectra $CDCl_3$ using a Brucker DPX spectrometer.

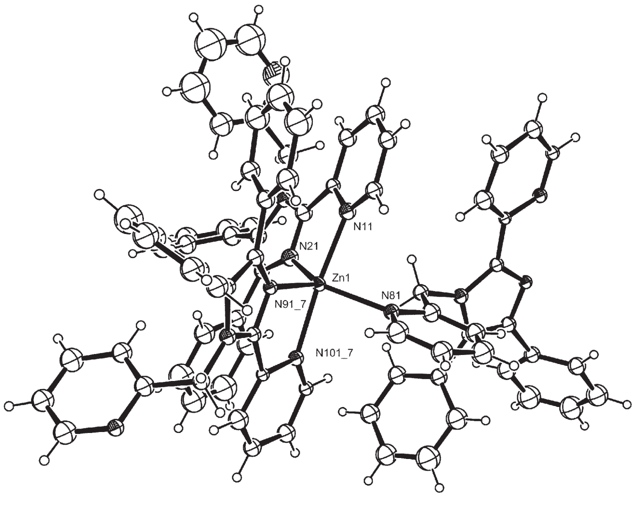


Fig. 3 The environment of one zinc atom in the polymeric cation in **2** with ellipsoids at 25% probability. Selected bond distances (Å) and angles (°): Zn1–N91_7 2.053(11), Zn1–N21 2.072(12), Zn1–N101_7 2.10(11), Zn1–N11 2.121(12), Zn1–N81 2.186(11), N91_7–Zn1–N21 115.7(5), N91_7–Zn1–N101_7 79.2(4), N21–Zn1–N101_7 101.8(5), N91_7–Zn1–N11 104.7(5), N91_7–Zn1–N11 79.4(5), N101_7–Zn1–N11 174.9(5), N91_7–Zn1–N81 112.7(4), N21–Zn1–N81 131.6(5), N101_7–Zn1–N81 86.4(4), N11–Zn1–N81 89.2(4). Symmetry operation 7 is $0.5-x,\ 0.5+y,\ 0.25-z$.

Syntheses

L. Benzil (2.04 g, 9.7 mmol) was dissolved in 30 ml of anhydrous methanol. To this solution, freshly distilled 2-(methylamino)pyridine (2 ml, 19.4 mmol) was added and refluxed for 5 h. Then the reaction mixture was evaporated at room temperature under reduced pressure to obtain a reddish yellow gum. It was dissolved in 50 ml of diethylether and filtered. The filtrate was left to stand in air. After complete evaporation of the solvent, a gummy reddish yellow mass was obtained, which was kept *in vacuo* over fused $CaCl_2$. Yield 2.60 g (69%).

ZnL′Cl₂ (1). Solid anhydrous zinc chloride (0.14 g, 1 mmol) was added to L (0.39 g, 1 mmol) dissolved in 30 ml of methanol and stirred for 1 h. The resulting red solution was kept in the refrigerator for 2 days. The red crystalline compound that precipitated was collected by filtration. Yield 0.41 g (80%). The crystals were suitable for X-ray crystallography. Anal. calcd for $C_{26}H_{20}N_4ZnCl_2$: C, 59.49; H, 3.84; N, 10.68; found: C, 59.47; H, 3.67; N, 10.58%. UV/VIS ($CHCl_3$) λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 343 (14 500), 256 (15 200). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 5.50 (s, methylene, 2H), 6.85–8.57 (aromatic, 18H).

L′. ZnL′Cl$_2$ (1.05 g, 2 mmol) was dissolved in 30 ml of chloroform. To this solution, 10 ml of 5 N aqueous NaOH was added and stirred for 90 min. The chloroform layer was washed thoroughly with water (20 ml × 3) and dried by adding anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure at room temperature to obtain a yellow gum. After keeping the gum *in vacuo* over fused $CaCl_2$ for several days, a yellow solid was obtained. Yield 0.59 g (18%). Anal. calcd for $C_{26}H_{20}N_4$: C, 80.38; H, 5.19; N, 14.43; found: C, 80.26; H, 5.11; N, 14.49%. UV/VIS ($CHCl_3$) λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 317 (22 900). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 5.90 (s, methylene, 2H), 6.77–8.42 (aromatic, 18H).

ZnL′Cl₂ by starting with L′. Solid anhydrous zinc chloride (0.03 g, 1 mmol) was added to L′ (0.08 g, 0.18 mmol) dissolved in 7 ml of methanol and stirred for 2 h. The resulting red solution was kept in air overnight. The red precipitate was filtered, washed first with 10 ml of water and then with 10 ml of *n*-hexane. It was dried *in vacuo* over fused $CaCl_2$. Yield 0.06 g (55%).

$[Zn(L')_2](ClO_4)_2\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}CH_2Cl_2$ (2). Solid $Zn(ClO_4)_2\cdot 6H_2O$ (0.09 g, 0.25 mmol) was added to L′ (0.19 g, 0.5 mmol) dissolved in 10 ml of tetrahydrofuran and stirred for 30 min. The resulting yellow solution was left in air for 2 h. The yellow precipitate was filtered, washed with 5 ml of water and dried *in vacuo* over fused $CaCl_2$. It was recrystallised from a 3:1 dichloromethane–petroleum ether mixture. Yield 0.16 g (61%). Colourless single crystals were grown by direct diffusion of petroleum ether into a dilute dichloromethane solution of the complex. Anal. calcd for $C_{52.5}H_{42}N_8ZnCl_3O_{8.5}$: C, 57.68; H, 3.88; N, 10.25; found: C, 57.79; H, 3.81; N, 10.31%. FTIR (KBr) ν/cm^{-1}: 1090vs, 623s (ClO_4). UV/VIS ($CHCl_3$) λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 329 (21 700), 254 (23 900). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 5.27 (s, methylene of CH_2Cl_2, 1H), 5.69 (br, methylene, 4H), 6.84–8.45 (br signals, aromatic, 36H).

CAUTION! Though we have not met with any incidents while working with **2**, care should be taken in handling it as perchlorates are potentially explosive. It should not be prepared and stored in large amounts.

X-Ray crystallography

For **1**, 4188 independent reflections were collected on an automatic four-circle Nicolet R3mV diffractometer at 293(2) K using graphite monochromated Mo-Kα radiation. The data were corrected for Lorentz polarisation effects and an empirical absorption correction applied. Data for **2** were measured at 293(2) K with MoKα radiation using the MARresearch Image Plate System. The crystal was positioned at 100 mm from the image plate and 100 frames were measured at 2° intervals with a counting time of 5 min. Data analysis for **2** was carried out with the XDS program[7] to provide 5426 independent reflections. Both the structures were solved using direct methods with the SHELXS-86 program.[8] The structure of **2** contains one water and one dichloromethane solvent molecule, both given 50% occupancy although for the latter there were three sets of chlorine atoms, each given 16.67% occupancy, which were refined with distance constraints. The high *R* values for **2** are due to the weak and distorted spot shapes obtained in the diffraction pattern. Indeed, the R_{int} value for 25 096 reflections was 0.1285. This made it necessary for only the zinc and chlorine atoms to be refined anisotropically. The hydrogen atoms in solvent molecules were not included in the analysis. Full-matrix least-squares refinement (based on F^2; SHELXL-93[9]) gave $R_1 = 0.0464$, $wR_2 = 0.1135$ [2960 reflections, $I > 2\sigma(I)$] for **1** and $R_1 = 0.1177$, $wR_2 = 0.2299$ [4806 reflections, $I > 2\sigma(I)$] for **2**. For all reflections $R_1 = 0.1102$, $wR_2 = 0.3237$ for **1** and $R_1 = 0.1366$, $wR_2 = 0.2402$ for **2**.†

Crystal data for ZnL′Cl₂ (1). $C_{26}H_{20}Cl_2N_4Zn$, $M_w = 524.7$, monoclinic, space group $P2_1/n$, $a = 15.777(3)$, $b = 10.409(2)$, $c = 15.932(3)$ Å, $\beta = 114.05(3)°$, $U = 2389(1)$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, $\mu = 1.27$ mm^{-1}.

Crystal data for $[Zn(L')_2](ClO_4)_2\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}CH_2Cl_2$ (2). $C_{52.5}H_{42}Cl_3N_8O_{8.5}Zn$, $M_w = 1092.66$, tetragonal, space group $P4_12_12$, $a = b = 16.513(18)$, $c = 39.02(4)$ Å, $U = 10640(20)$ Å^3, $Z = 8$, $D_c = 1.364$ g cm^{-3}, $\mu = 0.67$ mm^{-1}.

Acknowledgements

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† CCDC reference numbers 222262 and 222263. See http://www.rsc.org/suppdata/nj/b3/b308294f/ for crystallographic data in .cif or other electronic format.