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Synthesis and structural characterisation of novel bimetallic dipyrromethene complexes: rotational locking of the 5-aryl group

Jonathan M. Sutton,[a] Eleanor Rogerson,[b] Christopher J. Wilson,[b] Amanda E. Sparke,[b] Stephen J. Archibald*[b] and Ross W. Boyle*[b]

[a] *Argenta Discovery Ltd, 7-9 Spire Green Centre, Flex Meadow, Harlow, Essex, UK CM19 5TR*
[b] *Department of Chemistry, The University of Hull, Kingston upon Hull, UK HU6 7RX.*
E-mail: r.w.boyle@hull.ac.uk; Fax: +44 (0)1482 466410; Tel: +44 (0)1482 466353

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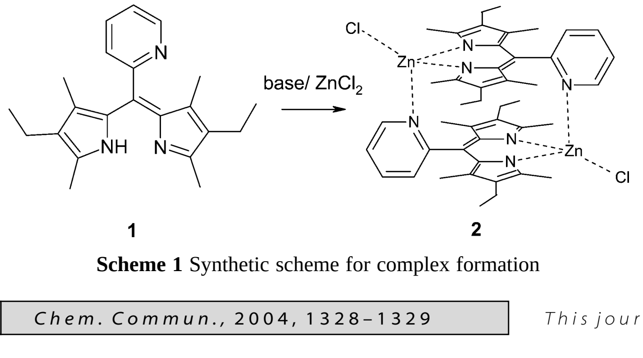
Complexation of 2,8-diethyl-1,3,7,9-tetramethyl-5-(2-pyridyl)-dipyrromethene with zinc(II) generated an unprecedented structural motif for a dipyrromethene ligand, of formula Zn_2(dipyrromethene)$_2X_2$, where X represents a coordinated anion.

Dipyrromethenes (or dipyrrins) are fully conjugated, highly coloured, planar molecules, which are known to readily coordinate to transition metals.[1–3] Dipyrromethene complexes with boron (BODIPY) have received considerable interest due to their relative ease of preparation and functionalisation, high extinction coefficients, high fluorescence quantum yields and excellent photostability.[4] These complexes have found applications as fluorescent probes and sensors,[5] laser dyes[6] and in optoelectric devices.[7]

Prior interest in dipyrromethene transition metal complexes for fluorescence applications has been limited as they form relatively 'non-fluorescent' monometallic bis or tris(dipyrromethene) complexes.[3, 8] However we, and others,[1] have recently found that restrictions on internal rotation of the aryl ring can alter excited state properties, leading to an increase in fluorescence quantum yields relative to the corresponding 5-phenyldipyrromethene complexes. We report here an unprecedented structure of the complex formed between a novel tridentate dipyrromethene ligand and zinc(II). The complex shows an enhanced fluorescence quantum yield relative to the corresponding complex formed by 5-phenyldipyrromethene and zinc(II), which is in accord with locking of the aryl group by a coordinate bond between the 2-pyridyl nitrogen and zinc. We also examine the possibility of coordinated anion metathesis.

There are only a few recent reports of transition metal complexes with dipyrromethene ligands and even more limited literature reporting dipyrromethene molecules bearing extra donor sites at the 5-position.[9] We have been investigating dipyrromethene complexes with a 5-(2-pyridyl) group as an additional donor site, resulting in a tridentate ligand. Due to the rigid nature of the dipyrromethene, the molecule cannot rearrange into an appropriate geometry for face capping coordination and therefore is likely to provide bridged structural motifs upon coordination to metal cations. However, Cohen and co-workers have recently reported a heteroleptic copper(II) dipyrromethene complex with a 5-(2-pyridyl) substituent that is surprisingly a discrete monomer with no coordination at the pyridyl nitrogen in the solid state structure.[10]

2,8-Diethyl-1,3,7,9-tetramethyl-5-(2-pyridyl)-dipyrromethene **1** was synthesised† by reaction of kryptopyrrole with the acid chloride of picolinic acid, which was generated *in situ*. Complexation with zinc chloride, in the presence of base, generated a neutral zinc complex **2** of empirical formula Zn(dipyrromethene)Cl. The complex was isolated as a dark red powder on evaporation of the solvent.‡ Recrystallisation from dichloromethane *via* diethyl ether diffusion gave crystals suitable for single crystal X-ray diffraction.§



Scheme 1 Synthetic scheme for complex formation

The structure of **2** shows the Zn_2(dipyrromethene)$_2Cl_2$ unit, where the zinc(II) ion is coordinated to two pyrrolic nitrogen atoms from one dipyrromethene and the pyridyl nitrogen atom from the second dipyrromethene forming a dimer, with the remaining coordination site occupied by the chloride. The zinc(II) ions are crystallographically inequivalent but show identical distorted tetrahedral coordination geometries. The dipyrromethene ligands bridge the two zinc ions to give a Zn–Zn intramolecular distance of 5.2822(6) Å. The zinc cation to pyrrolic nitrogen atom bonds are similar in length to known monomeric structures with dipyrromethene type ligands (observed range 1.958–1.996 Å).[11] As mentioned previously, dipyrromethene ligands have frequently been observed to form monomeric complexes with 2 : 1 or 3 : 1 dipyrromethene to metal ratios. A search of the CSD reveals our structure, with a 1 : 1 ratio of dipyrromethene to zinc(II), as the only deposited example of a dipyrromethene ligand bridging two metal centres.[12]

The fluorescence quantum yield (Φ_f) for **2** is 0.057 in dichloromethane. The only literature compounds available for comparison are the Zn(dipyrromethene)$_2$ complexes synthesised by Lindsey and co-workers.[1] The rotationally restricted 5-mesityl derivative shows a considerably higher quantum yield than the 5-phenyl derivative (Φ_f = 0.36 and 0.006 respectively). Our dimeric complex lies between these values but would ideally be compared with a similarly alkylated 5-phenyldipyrromethene complex to reflect the steric contribution to rotational locking.

One aspect of our fluorescent zinc complex of particular interest is the potential for exchange of the non-pyrrole/pyridyl site on the metal centre. Such a mechanism would open up the possibility for formation of supramolecular structures and allow us to probe the effects of the anion on the photophysical properties. We found that

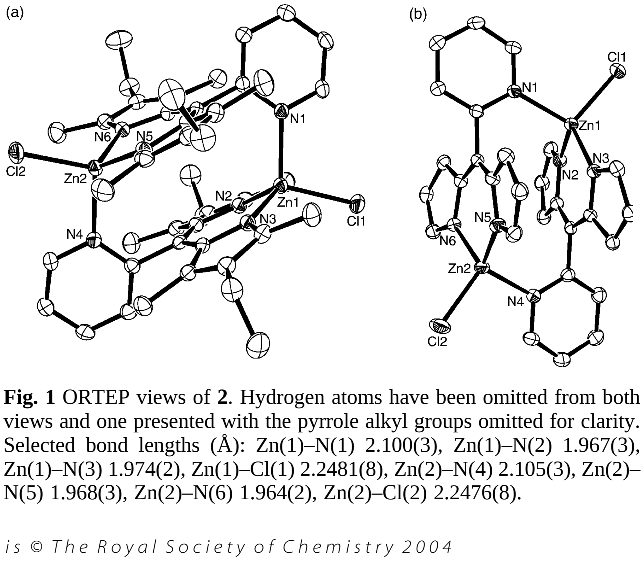


Fig. 1 ORTEP views of **2**. Hydrogen atoms have been omitted from both views and one presented with the pyrrole alkyl groups omitted for clarity. Selected bond lengths (Å): Zn(1)–N(1) 2.100(3), Zn(1)–N(2) 1.967(3), Zn(1)–N(3) 1.974(2), Zn(1)–Cl(1) 2.2481(8), Zn(2)–N(4) 2.105(3), Zn(2)–N(5) 1.968(3), Zn(2)–N(6) 1.964(2), Zn(2)–Cl(2) 2.2476(8).

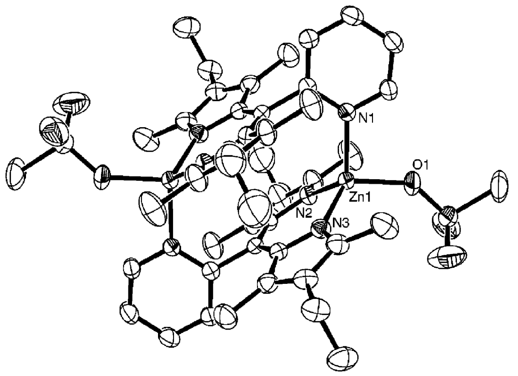


Fig. 2 ORTEP view of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Zn(1)–N(1) 2.047(2), Zn(1)–N(2) 1.954(2), Zn(1)–N(3) 1.949(2), Zn(1)–O(1) 1.956(2).

the coordinated chloride can be quantitatively exchanged with a variety of anions by mixing **2** with the appropriate silver(I) salt in ethanol and filtering off the precipitated silver chloride. For example: dark red **3** was isolated and further purified by precipitation with diethyl ether.¶ This particular complex was further characterised by X-ray crystallography showing an almost identical structure to that already observed, with a monodentate methane sulfonate replacing the chloride anion.§ The Zn–Zn distance is very similar to the chloride structure at 5.1199(9) Å. It is also interesting to note the additional symmetry in this structure, with a Zn(dipyrromethene)(CH_3SO_3) moiety forming the asymmetric unit. The twist angles of the pyridyl ring plane relative to the plane formed by the two pyrrole rings were determined for each structure; 83.22(9) and 78.45(10)° for **2**, and 83.78(9)° for **3**.

This zinc complex, with the more weakly coordinated methylsulfonate anion, shows a considerable affinity for chloride. Chloride was abstracted from both dichloromethane and chloroform solutions on standing. The exchange for chloride was confirmed by ^{1}H NMR spectroscopy and single crystal X-ray diffraction.

These results show an alternative route to rotational restriction of the 5-aryl group in dipyrromethene complexes and suggest possibilities for tuning of the photophysical properties. The presence of a monodentate anion in the coordination sphere of the tetrahedrally coordinated zinc will allow investigation of the effects of variation at this site. Such studies are under way, including an investigation of excited state lifetimes, and are being performed in conjunction with complexation reactions to probe the structural motifs formed with other metal centres.

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Notes and references

† Preparation of **1**. Freshly distilled $POCl_3$ (1.75 ml, 18.8 mmol) was slowly added to a stirred solution of 2-picolinic acid (0.25 g, 2.03 mmol) and 2,4-dimethyl-3-ethylpyrrole (0.50 g, 4.06 mmol) in chloroform (50 ml) under nitrogen. The solution was heated at reflux for 16 h and then the solvent evaporated *in vacuo*. The resulting oil was dissolved in chloroform and washed with concentrated aqueous ammonia. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo* to give a dark green iridescent powder. The product was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, 1H, pyridyl), 7.74 (t, 1H, pyridyl), 7.42 (d, 1H, pyridyl), 7.34 (t, 1H, pyridyl), 2.32 (s, 6H, Me), 2.26 (q, 4H, CH_2), 1.11 (s, 6H, Me) and 0.96 (t, 6H, Me). *m*/*z* (EI) 333 (M^+), 318 (M − Me), 289 (M − Et, Me), 274 (M − Et, 2Me).

‡ Preparation of **2**. **1** (1.83 g, 5.48 mmol) was dissolved in methanol (40 ml). Conc. NH_3 (4 drops) was added followed by $ZnCl_2$ (0.82 g, 6.04 mmol) in methanol (5 ml). The solution was stirred overnight and the product filtered off to yield 1.00 g (42%) dark red solid. Dark coloured iridescent crystals of **2** were grown from diethyl ether diffusion into DCM solution. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (d, 1H, pyridyl), 7.99 (t, 1H, pyridyl), 7.73 (t, 1H, pyridyl), 7.57 (d, 1H, pyridyl), 2.18 (s, 6H, Me), 2.04 (m, 4H, CH_2) and 0.81 (s, 12H, Me). Calc. for $C_{44}H_{52}Cl_2N_6Zn_2$: C, 60.98; H, 6.05; N, 9.70%. Found: C, 60.92; H, 6.10; N, 9.85%. UV-vis. (CH_2Cl_2) λ_{max} = 474 nm ($\varepsilon \approx$ 52,000 $M^{-1}cm^{-1}$). Fluorescence quantum yield (λ_{ex} = 474 nm, λ_{em} = 523 nm) was determined using fluorescein as standard.[13]

§ Crystal data for **2**. Et_2O: $C_{44}H_{52}Cl_2N_6Zn_2.(C_2H_5)O$, $T = 150(2)$ K, monoclinic, $P21/n$, $a = 11.4184(12)$, $b = 24.785(4)$, $c = 16.7968(17)$ Å, $\beta = 106.345(8)°$, $V = 4561.4(9)$ Å^3, $Z = 4$, $F(000) = 1976$, 56160 reflections measured of which 19879 were independent on F^2, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0477$, $wR2 = 0.0970$, R indices (all data): $R1 = 0.1762$, $wR2 = 0.1255$.

Crystal data for **3**: $C_{46}H_{58}N_6O_6S_2Zn_2$, $T = 150(2)$ K, monoclinic, $P21/n$, $a = 12.9671(19)$, $b = 8.9847(8)$, $c = 19.804(3)$ Å, $\beta = 98.061(11)°$, $V = 2286.1(5)$ Å^3, $Z = 2$, $F(000) = 1032$, 28786 reflections measured of which 8884 were independent on F^2, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0548$, $wR2 = 0.1381$, R indices (all data): $R1 = 0.0987$, $wR2 = 0.1532$.

Both structures were solved by direct methods (SHELXS) and refined against F^2 (SHELX97) using WinGX.[14] CCDC 23450 and 234541. See http://www.rsc.org/suppdata/cc/b4/b404147j/ for crystallographic data in .cif or other electronic format.

¶ Preparation of **3**. **2** (0.50 g, 1.15 mmol) was dissolved in ethanol (50 ml) and AgO_3SMe (0.47 g, 2.30 mmol) added. The mixture was stirred overnight then filtered. The solvent was removed from the filtrate to give dark red **3**, yield 0.56 g (100%). Dark coloured iridescent crystals of **3** were grown by the same method as **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, 1H, pyridyl), 7.77 (t, 1H, pyridyl), 7.48 (d, 1H, pyridyl), 7.37 (t, 1H, pyridyl), 2.65 (br, 3H, SO_3CH_3), 2.25 (m, 4H, CH_2), 2.01 (s, 3H, CH_3), 1.96 (s, 3H, Me), 1.09 (s, 6H, Me), 0.91 (m, 6H, Me).

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