

## The Crystal and Molecular Structure of Dichloro(3,3'-dimethyl-2,2'-bi-indazole)zinc: First Example of a 2,2'-Bipyridine-like Cyclic 2 : 2 Complex

Juan-Carlos Cuevas,<sup>a</sup> Javier de Mendoza,<sup>\*a</sup> Pilar Prados,<sup>a</sup> Félix Hernández-Cano,<sup>b</sup> and Concepción Foces-Foces<sup>b</sup>

<sup>a</sup> Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

<sup>b</sup> Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006-Madrid, Spain

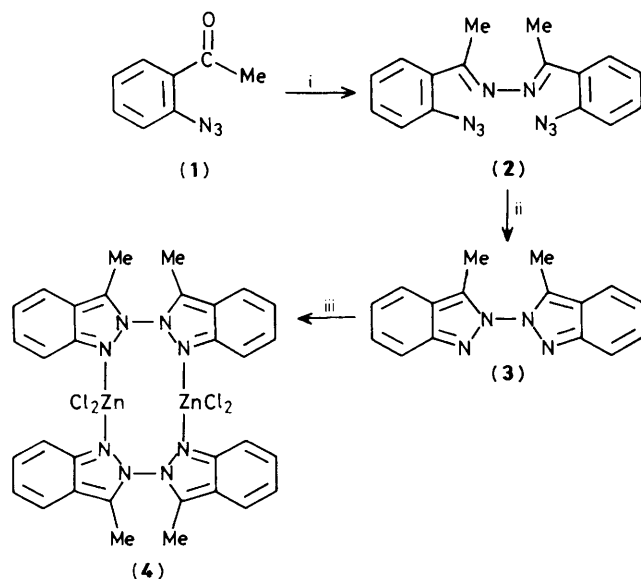
An X-ray structure determination of the chloroform solvate of the complex formed from ZnCl<sub>2</sub> and 3,3'-dimethyl-2,2'-bi-indazole has shown a dimeric cyclic structure incorporating two Zn atoms in a ten-membered ring with quasi two-fold symmetry, which leaves a central hole of 3.2 × 2.9 Å approximate dimensions.

Despite the great interest in transition metal complexes of 2,2'-bipyridine, 1,10-phenanthroline, and other related neutral bidentate ligands, comparatively little work has been performed with sterically hindered bipyridines, where complexation has been hampered either by direct interaction of substituents with the metal neighbourhood (as in 6,6'-dimethyl-2,2'-bipyridines), or by the coplanarity of the pyridine rings required for chelation being prevented (as in 3,3'-dimethyl-2,2'-bipyridines).

The only structural data so far available for 3,3'-dimethyl-2,2'-bipyridines concern methylmercury(II) complexes, for which a co-ordination of Hg to only one nitrogen has been shown, with weak  $\pi$ -interaction to the second aromatic ring.<sup>1</sup> More recently, Rebek *et al.* have reported a (1:1) Zn<sup>II</sup> complex, on the basis of microanalytical data, but no evidence was presented to ascertain the exact (1:1) or (2:2) stoichiometry of the complex.<sup>2</sup>

Owing to our interest in the incorporation of *N,N'*-linked biazole systems into ligands for metal co-ordination,<sup>3</sup> we focused our attention on 3,3'-dimethyl-2,2'-bi-indazole (3). We reasoned that, besides the presence of the methyl groups, the known tendency of *N,N'*-linked biazoles to be in a non-planar, quasi orthogonal conformation<sup>4</sup> would effectively prevent the formation of (1:1) complexes, favouring the unusual (2:2) mode of co-ordination.

The ligand (3) (colourless crystals, 83%, m.p. 143–144 °C) and its zinc complex (4) (m.p. >300 °C) were obtained from



Scheme 1. i, N<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>O, HCl, EtOH, 12 h, room temp.; ii, C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>-1,2, 2 h, 150 °C; iii, ZnCl<sub>2</sub>, EtOH, 1 h, room temp.

(1)<sup>5</sup> as shown in Scheme 1, *via* azine (2) (yellow needles, 86%, m.p. 120–121 °C).<sup>†</sup>

As expected, the structure of (4) consisted of dimers of 3,3'-dimethyl-2,2'-bi-indazole, which have a pseudo-binary symmetry axis through each of them (Figure 1).<sup>‡</sup> The four fused rings of each dimer adopt a conformation with

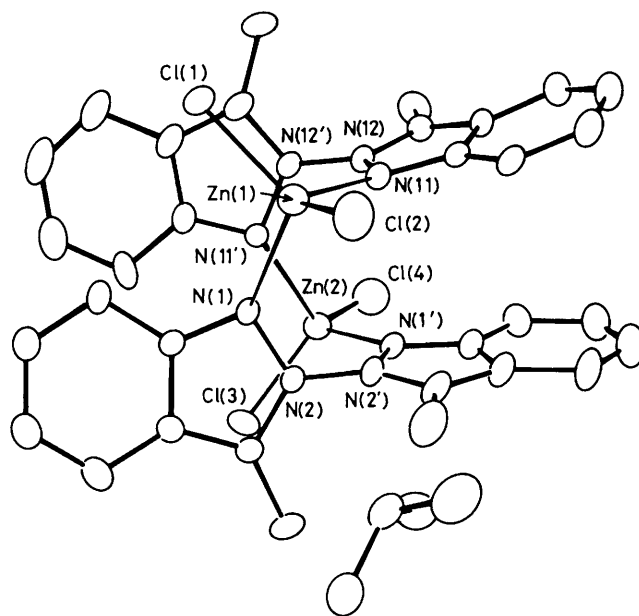
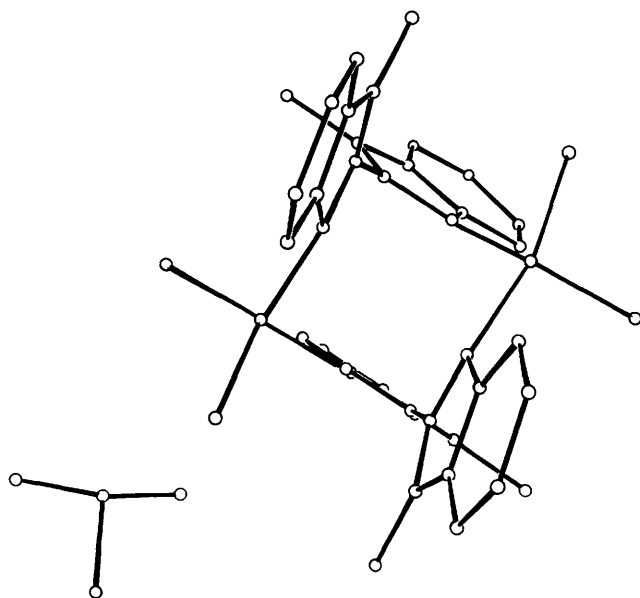


Figure 1. Molecular structure of the Zn<sup>II</sup> complex (4). Selected bond distances (Å): Zn(1)–Zn(2), 4.530(1); Zn(1)–Cl(1), 2.219(1); Zn(1)–Cl(2), 2.210(2); Zn(1)–N(1), 2.063(4); Zn(1)–N(11), 2.060(4); Zn(2)–Cl(3), 2.220(2); Zn(2)–Cl(4), 2.203(2); Zn(2)–N(1'), 2.057(4); Zn(2)–N(11'), 2.046(4); N(2)–N(2'), 1.367(6); N(12)–N(12'), 1.382(6).

<sup>†</sup> Satisfactory microanalytical data, as well as i.r., n.m.r. (<sup>1</sup>H and <sup>13</sup>C), and mass spectra were obtained for the new compounds (2), (3), and (4).

<sup>‡</sup> Crystal data for (4): C<sub>32</sub>H<sub>28</sub>N<sub>8</sub>Zn<sub>2</sub>Cl<sub>4</sub>·CHCl<sub>3</sub>, triclinic, space group P $\bar{1}$ ,  $a = 15.3221(8)$ ,  $b = 11.8450(5)$ ,  $c = 10.9590(5)$  Å;  $\alpha = 104.314(4)$ ,  $\beta = 93.837(4)$ ,  $\gamma = 92.763(5)^\circ$ ;  $Z = 2$ ,  $D_c = 1.585$  g cm<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha) = 64.68$  cm<sup>-1</sup>, after absorption correction. A rhombic prismatic, transparent colourless crystal of 0.60 × 0.47 × 0.47 mm was used to collect 6516 independent data on a Philips PW 1100 diffractometer. The structure was solved by direct methods and refined to an  $R$  index of 0.065, using 5729 observed reflections [ $I/\sigma(I) > 3.0$ ]. The final difference map showed a peak of 0.95 e Å<sup>-3</sup>. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.



**Figure 2.** Molecular structure of (4). Perspective view showing the central ten-membered ring. Dihedral angles ( $^{\circ}$ ): N(2')-N(2)-N(1)-Zn(1),  $-21.2(5)$ ; N(2)-N(1)-Zn(1)-N(11),  $53.5(4)$ ; N(1)-Zn(1)-N(11)-N(12),  $70.1(4)$ ; Zn(1)-N(11)-N(12)-N(12'),  $-6.8(5)$ ; N(11)-N(12)-N(12')-N(11'),  $-69.8(5)$ ; N(12)-N(12')-N(11')-Zn(2),  $-34.4(4)$ ; N(12')-N(11')-Zn(2)-N(1'),  $64.7(3)$ ; N(11')-Zn(2)-N(1')-N(2'),  $67.4(4)$ ; Zn(2)-N(1')-N(2')-N(2),  $-5.1(6)$ ; N(1')-N(2')-N(2)-N(1),  $-77.9(5)$ .

4-symmetry, distorted as they hang from a ten-membered ring. They leave a central hole, quasi rectangular in shape, of approximate dimensions  $3.3 \times 2.9 \text{ \AA}$  (Figure 2). The pseudo two-fold axis of symmetry becomes less well defined the further away from the centre of the ten-membered ring. Both Zn atoms are co-ordinated in a distorted manner, with the Cl-Zn-Cl angles [ $113.0(1)$ ,  $113.7(1)^{\circ}$ ] greater than those for N-Zn-N [ $104.7(2)$ ,  $103.2(2)^{\circ}$ ]. The tetrahedrons are at almost  $90^{\circ}$  to each other.

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