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# Low-energy Barrier to Intramolecular Inversion of Tetrahedral Configuration at a $Zn^{II}$ Centre

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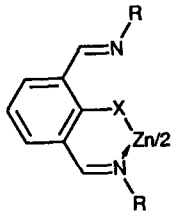
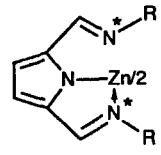
The associative inner-nucleophile assisted mechanism of inversion of tetrahedral configuration at the metal centre in bis-chelate $Zn^{II}$ complexes based on alterdentate ligands, *N*-alkylimines of 2,5-diformylpyrrole, has been proved by dynamic $^{1}H$, $^{13}C$, $^{15}N$ NMR spectroscopic and X-ray crystallographic studies.

Complexes of $Zn^{II}$ display stereochemical nonrigidity[1,2] and unusual coordination flexibility,[3] properties which are deemed to be instrumental in allowing these to function as efficient catalysts for a variety of biologically important reactions. In order to model some underlying features of the intricate mechanisms governing these processes a systematic study of ligand exchange reactions and intramolecular inversion of tetrahedral configuration at a $Zn^{II}$ centre, readily occurring in solution, has been undertaken.[1,2,4,5] Thus, by studying the dynamic $^{1}H$ and $^{13}C$ NMR spectral behaviour of bis-chelate $Zn^{II}$ complexes **1** derived from alterdentate[6] ligands (bis-imines of 2,6-diformylphenols and thiophenols), it was possible to observe separately two competitive processes leading to inversion of stereochemical configuration at $Zn^{II}$: (i) a digonal-twist polytopal rearrangement through the square-planar $Zn^{II}$ species and (ii) a Zn—N bond-breaking process followed by a

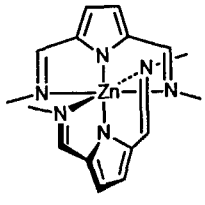
random recombination involving either of the nitrogen ligating centres of the alterdentate ligand. The energy preference for one of these pathways was found to be extremely sensitive to the type of ligand environment; in particular, to the origin of the ligating atom X.[5]



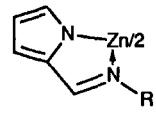
**1a** X = O
**1b** X = S



**2a** R = Pr$^i$
**2b** R = c-$C_6H_{11}$
**2c** N* = $^{15}$N, R = c-$C_6H_{11}$



**3**



**4** R = c-$C_6H_{11}$

Here we report on the synthesis and investigation into the molecular structure and fluxionality of novel bis-chelate complexes of Zn$^{II}$ **2** based on different alterdentate ligands, bis-imines of 2,5-diformylpyrrole. In contrast to complexes **1**, whose spatial structure warrants engaging into coordination with the metal centre of only one of the imine moieties of the ligands, in **2** both hexa- and penta-coordinated Zn$^{II}$ structures, **3** and **5** respectively, are virtually unhindered. Such a structural peculiarity of complexes **2** provides the possibility of an inner-nucleophile assisted associated mechanism of inversion of stereochemical configuration at a tetracoordinated Zn$^{II}$ centre to be operating in addition to the mechanisms revealed in the case of complexes **1**. Indications to the efficiency of the nucleophile assisted pathways of inversion of tetrahedral configuration at Si, Ge and Sn centres may be found in the literature.[7,8]

Both $^1$H and $^{13}$C NMR spectra of complexes **2** display their extremely high fluxionality in solution. Fig. 1 portrays the $^1$H NMR spectrum of **2a** which features the effective $D_{2d}$ symmetry of the molecule which it retains even at a solution temperature as low as 193 K. The protons of the diastereotopic methyl groups of two pairs of prochiral isopropyl substituents (at coordinated and noncoordinated centres) in **2a** show one sharp common signal, thus indicating either an achiral hexacoordinated structure **3** or a very rapid process of inversion of

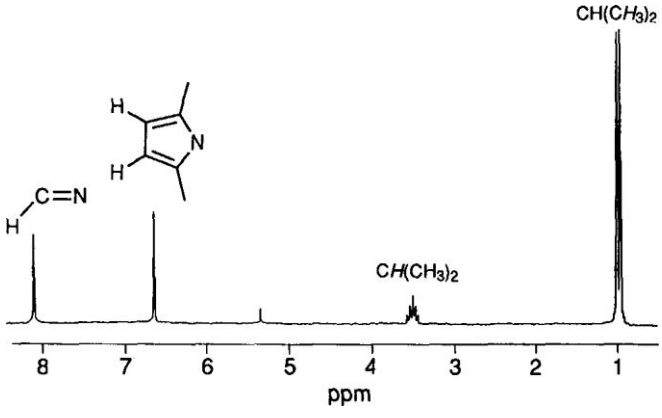



**Fig. 1** $^1$H NMR spectrum (300 MHz) of complex **2a** in $CD_2Cl_2$ solution at 203 K

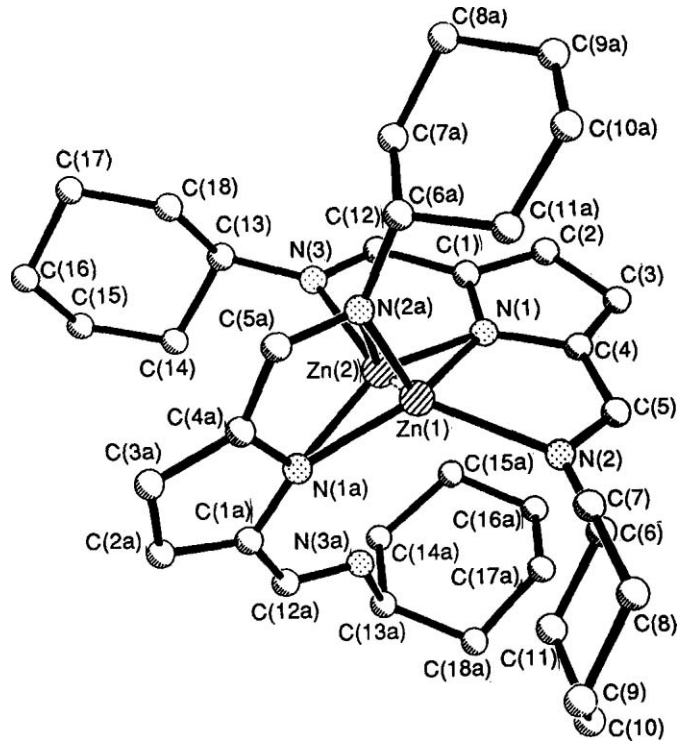



**Fig. 2** Structure of complex **2b** at 298 K. Selected bond lengths/Å and angles/°: Zn(1)—N(1) 1.93(5); Zn(1)—N(2) 2.157(5); Zn(1)—N(1a) 1.965(5); Zn(1)—N(2a) 2.139(4); Zn(1)—N(3) 3.010(6); Zn(2)—N(1) 1.911(6); Zn(2)—N(3) 2.290(7); Zn(2)—N(1a) 1.911(7); Zn(2)—N(2a) 2.094(8); Zn(2)···N(2) 2.982(8); N(2)—Zn(1)—N(3) 144.2(2); N(2)—Zn(2)—N(3) 144.8(3)

configuration at the Zn$^{II}$ centre. The spectral pattern is not affected by variation in concentration of the solution.

In the case of the symmetrical structure **3**, complexes **2** would possess zero dipole moment values. However, the magnitude of the dipole moment of **2b** determined in benzene solution by use of the standard heterodyn technique was found to be 3.17 D, which is close to that (3.66 D) of bis(2-pyrrolaldiminato)zinc(II) **4**, apparently with a tetrahedral structure.

A single crystal X-ray diffraction study† of the structure of **2b** helped to clarify the origin of the extreme stereochemical nonrigidity of complexes **2** in solution. The central Zn$^{II}$ atom was found to be disordered on two unequally populated positions within a molecular cavity bound by heterocyclic and imine nitrogens. These are indicated in Fig. 2 as Zn(1) and Zn(2).

In each of the arrangements the Zn$^{II}$ atom possesses a distorted trigonal bipyramidal configuration, with the N(2) and N(3) atoms of the imine groups attached to the common pyrrole ring taking axial positions. By scanning the temperature of the crystal, the population of two arrangements of the central atom were varied as given below, the rest of the molecular geometry remaining practically unaffected.

| $T$/K | 353 | 298 | 223 | 143 |
|---|---|---|---|---|
| Zn(1) | 0.72 | 0.75 | 0.86 | 0.94 |
| Zn(2) | 0.28 | 0.25 | 0.14 | 0.06 |

These data suggest a dynamic character of the molecular disordering, the origin of which may be attributed to the $S_N2$-type intramolecular process of inversion of configuration

† Complexes **2** were prepared by coupling the respective *N*,*N*-dialkylimines with zinc acetate in methanol solution followed by recrystallization from hexane, m.p. **2a** 154–155°C; **2b** 153–154°C. Both compounds gave satisfactory analytical and spectral data.

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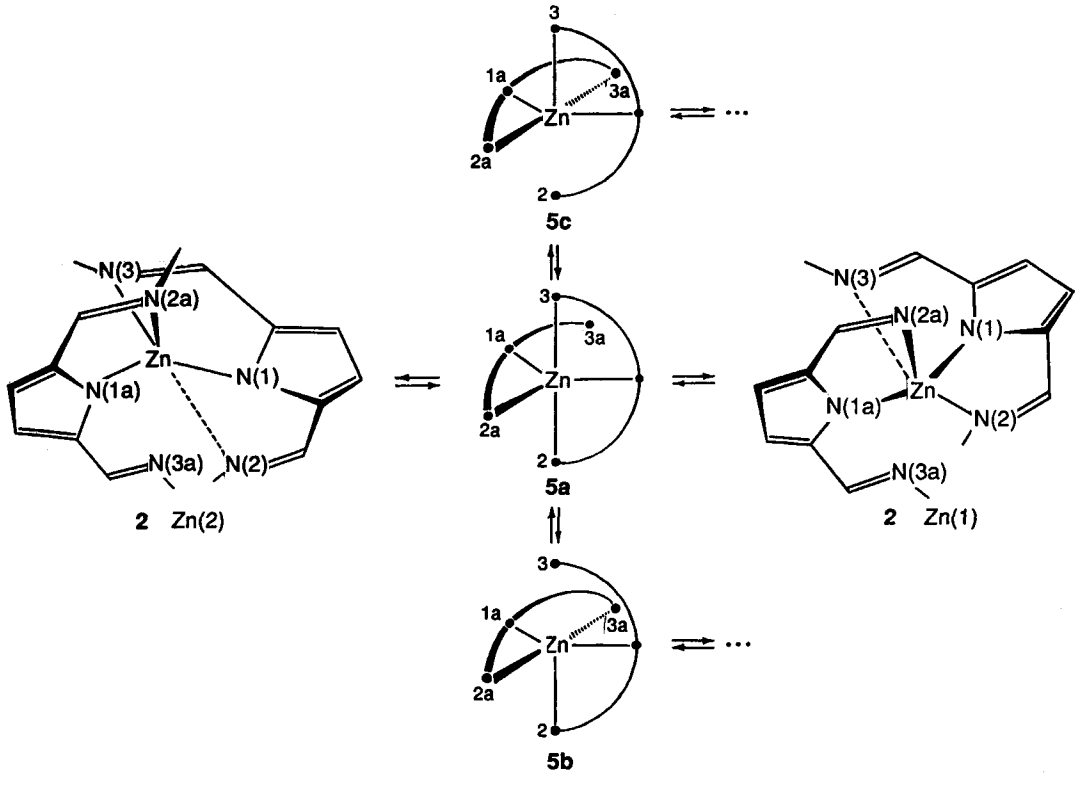


**Scheme 1**

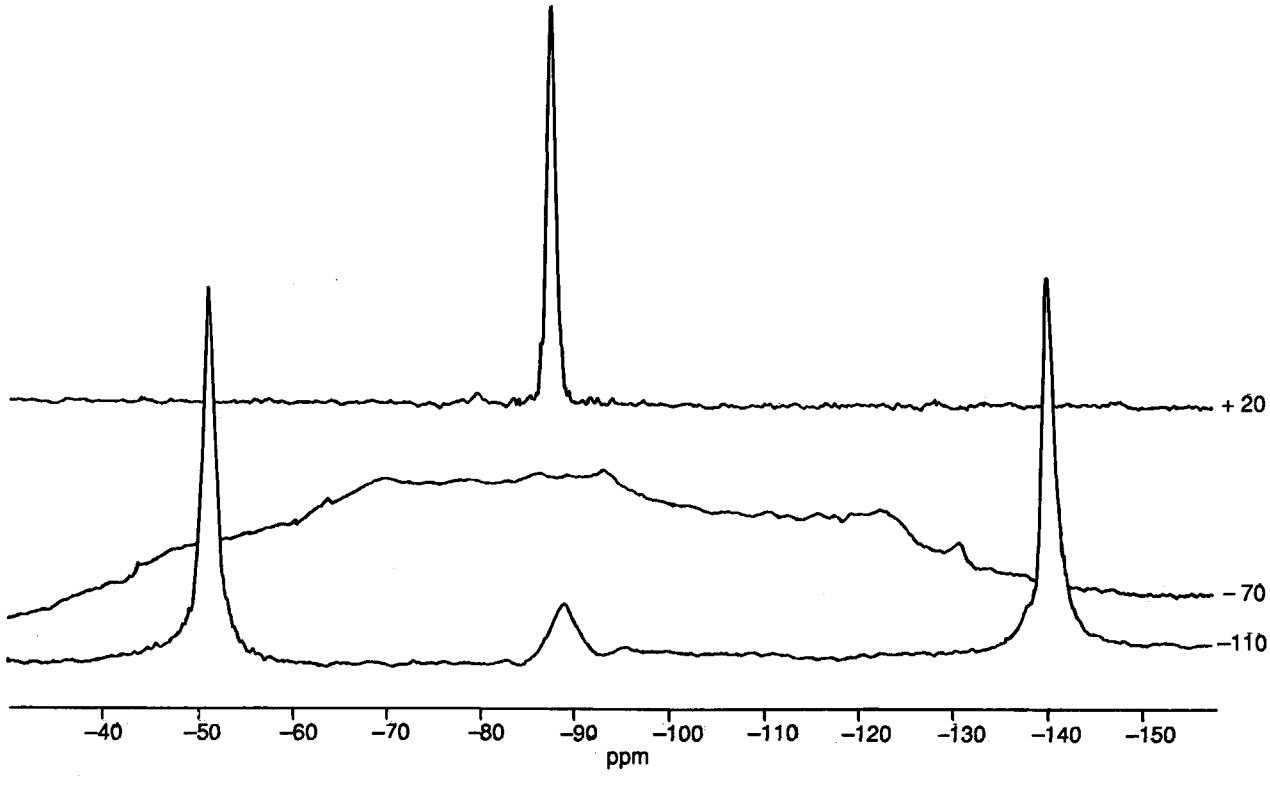


**Fig. 3** Temperature dependence of $^{15}N$ NMR spectra (30.4 MHz) of complex **2c** (95% enrichment in $^{15}N$ at imine nitrogens) in $CD_2Cl_2$–$Et_2O$ (7:3) solution. Chemical shifts are referred to $NO_3^-$ standard

at a tetrahedral $Zn^{II}$ centre due to the degenerate exchange reaction as featured to Scheme 1.

In this way the total averaging of signals belonging to all four azomethine groups occurs as evidenced by respective dynamic NMR spectra. By lowering the temperature of a $CD_2Cl_2$–$Et_2O$ (7:3) solution of **2b**, isotopically labelled by $^{15}N$ at the imine nitrogens, it was possible to observe coalescence of the $^{15}N$ signals from the pairs of coordinated (−140.1 ppm) and non-coordinated (−51.2 ppm) ligating atoms (Fig. 3) and to calculate the energy barrier to the inversion process: $\Delta G^{\ddagger}_{203} = 8.6$ kcal mol$^{-1}$.

When the process is frozen on the $^{15}N$ NMR time scale, an additional peak appears (at −88.2 ppm) which may be plausibly assigned to a small amount (*ca.* 10%) of the intermediate **5**.

‡ *Crystal data* for **2b** $(C_{18}H_{26}N_3)_2Zn$ at 298 K: monoclinic, space group $P2_1/c$, $a = 13.583(3)$ Å$^3$, $z = 4$, $d = 1.192$ g cm$^{-3}$. A total of 2296 independent reflections ($F > 6\sigma$) were measured by use of a Siemens P3 automatic diffractometer, monochromatized Mo–Kα radiation, $\theta/2\theta$ scan, $2\theta \leq 45°$. The structure was solved by direct method and refined by full-matrix least-squares in anisotropic approximation (isotropic for H atoms). Final *R*-factor was 4.6 ($R_w = 4.6$), $\Delta\rho_{max} = -0.35$ e Å$^3$.

Atomic coordinates, bond lengths and angles, and thermal parameters for the structure **2b** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *Mendeleev Commun.*, 1993, issue 1.

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