Syntheses and Characterization of Neutral Complexes of Zn(II) with Mono- and Dianionic Pyrrole-2-imine Ligands [(pyrrole-2-CH=N)$_n$–R]$^{n-}$ (n = 1, 2)

GERARD C. VAN STEIN, GERARD VAN KOTEN*, HANS PASSENIER, OLAV STEINEBACH and KEES VRIEZE

Laboratorium voor Anorganische Chemie, University of Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received February 3, 1984

The reactions of the dianionic [(pyrrole-2-CH= N)$_2$–R]$^{2-}$ ligands [(N$'_2$N$_2$)$^{2-}$] (R = (R)(S)-1,2-cyclohexane or 1,2-ethane) with Zn(II) yield neutral dimeric [Zn$_2$(N$'_2$N$_2$)$_2$] complexes. The dimeric nature of the complexes was established by field-desorption mass spectrometry. ^{1}H NMR studies show that these complexes have dimeric structures in solution in which the (N$'_2$N$_2$)$^{2-}$ ligands act as di-bidentates.

The metal centres have tetrahedral geometries and both have Δ or Λ configurations. The complex with the (R)(S)-1,2-cyclohexanediyl bridges has a rigid structure in solution. Neither intermolecular nor intramolecular exchange processes are observed. The ^{1}H NMR spectrum of the complex with the 1,2-ethanediyl bridging groups shows that at 213 K in CDCl$_3$ a fast conformational movement is already taking place between two identical structures of the complex. It is not possible to determine whether in this complex intermolecular exchange processes are also taking place.

The reactions of anionic [pyrrole-2-CH=N–R']$^-$ ligands [(N'N)$^-$] (R' = t-Bu, i-Pr, (S)-CHMePh or 2,6-xylyl) with Zn(II) yield the neutral Zn(N'N)$_2$ complexes. These complexes were synthesized to study the coordination properties of the [pyrrole-2-CH= N-R']$^-$ moieties with Zn(II). A ^{1}H NMR study established that the zinc centres in the complexes containing the prochiral i-Pr or chiral (S)-CHMePh substituents have tetrahedral geometries with Δ or Λ configurations in CDCl$_3$ at 213 K. These complexes undergo an intramolecular exchange process at higher temperatures (above 260 K when R' = i-Pr) which involves inversion of the configuration of the zinc centre. A mechanism for this exchange process is proposed.

Introduction

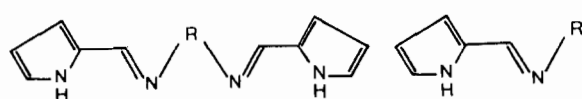To understand the reactivities of open-chain tetra-pyrrole pigments in the presence of metal centres

Fig. 1. Schematic representation of the H$_2$N$'_2$N$_2$ ligand (left) R = (R)(S)-1,2-cyclohexane (1) or 1,2-ethane (2) and of the HN'N ligand system (right) R' = t-Bu (3), i-Pr (4), (S)-CH-MePh (5) or 2,6-xylyl (6).

it is important to study the structural features of such metal complexes in more detail both in the solid (X-ray) and in solution (NMR, EPR). Recently Sheldrick and Engel published the X-ray structure of a zinc(II) biladiene-a,c complex [1]. The complex with 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-a,c has a bis-helical dimeric structure in which the two ligands coordinate to the zinc(II) centres as bridging di-bidentates and in which the metal centres have tetrahedral geometries. However, no information is available concerning the structure and dynamic behaviour in solution of such zinc(II) complexes. In order to study the latter aspect we have prepared the zinc(II) complexes with the H$_2$N$'_2$N$_2$ ligands (Hpyrrole-2-CH=N)$_2$-R (R = (R)(S)-1,2-cyclohexane or 1,2-ethane, see Fig. 1) as models and studied these complexes by ^{1}H NMR spectroscopy.

The H$_2$N$'_2$N$_2$ ligand system contains after deprotonation two anionic 'outer' (pyrrole)-N atoms which can bind to a metal centre *via* covalent N-M bonds and two neutral 'inner' (imine)-N atoms which can coordinate to the metal centre via donative N–M interactions. The stereochemistry of the R group connecting the two Hpyrrole-2-CH=N units can be changed and therefore its influence on the coordination properties can be studied.

We have also prepared the neutral Zn(N'N)$_2$ complexes derived from the HN'N ligands Hpyrrole-2-CH=N-R' (see Fig. 1). Such 2/1 ligand-to-metal complexes can provide information on the coordination behaviour of the monoanionic pyrrole-imine moieties with zinc(II) in solution and show how two such bidentates present in the (N$'_2$N$_2$)$^{2-}$ dianions cooperate when they bind to the metal centres. Holm *et al.* [2] have already shown that neutral M^{II}(N'N)$_2$ (M^{II} = Co, Cu or Ni) complexes of the

bidentate monoanionic [pyrrole-2-CH=N-R']⁻ ligands with tetrahedral geometries exist in two enantiomeric forms with the metal centres having either Δ of Λ** configurations.

In this paper we report the syntheses and characterization of the new zinc(II) complexes with the dianionic [(pyrrole-2-CH=N)$_2$-R]$^{2-}$ ligands where R is $(R)(S)$-1,2-cyclohexane and 1,2-ethane, and the monoanionic [pyrrole-2-CH=N-R']$^-$ ligands where R' is t-Bu§, i-Pr§, (S)-CHMePh or 2,6-xylyl. Based on the ^{1}H NMR results the structural features of the Zn(N'N)$_2$ complexes are discussed and a mechanism is proposed for the observed exchange process involving inversion of the configuration of the tetrahedrally surrounded Zn(II) centre.

Experimental

Preparation of the Compounds

All reactions were carried out under a nitrogen atmosphere in freshly distilled solvents. Pure $(R)(S)$-1,2-diaminocyclohexane was separated from the commercially available mixture of cis-$[(R)(S)]$ and trans-$[(R)(R),(S)(S)]$ isomers as described in the literature [4]. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, T.N.O., Utrecht (The Netherlands).

The Ligands

(R)(S)-1,2-(Hpyrrole-2-CH=N)₂-cyclohexane, 1

A solution of $(R)(S)$-1,2-diaminocyclohexane (10 mmol) in diethyl ether (50 ml) was added to a solution of Hpyrrole-2-carbaldehyde (20 mmol) in diethyl ether (100 ml). The solution was stirred for 19 h and then dried on Na$_2$SO$_4$. The Na$_2$SO$_4$ was filtered off and the filtrate concentrated to dryness at low pressure affording a light yellow powder. Crystallization from methanol at 233 K afforded pure crystals of 1 in 90% yield.

1,2-(Hpyrrole-2-CH=N)₂-ethane, 2

A solution of 1,2-diaminoethane (10 mmol) in diethyl ether (20 ml) was added to a solution of H-pyrrole-2-carbaldehyde in diethyl ether (100 ml). The solution was stirred for 19 h, during which time a white solid slowly precipitated. The solvent was decanted and the precipitate washed with diethyl ether (3 × 20 ml). Pure 2 was obtained by recrystallization from hot methanol in almost quantitative yields.

**For the explanation of the abbreviations Δ and Λ see reference 3.

§The syntheses of these complexes have been reported before by Holm *et al.* [2].

Hpyrrole-2-CH=N-R' (R' = t-Bu, 3; i-Pr, 4)

A solution of R'NH$_2$ (15 mmol) in diethyl ether (40 ml) was added to a solution of Hpyrrole-2-carbaldehyde in diethyl ether (40 ml). The reaction mixture was stirred for 19 h., dried on Na$_2$SO$_4$, and then filtered. The solvent was evaporated from the filtrate yielding (90%) a yellow liquid which was distilled at low pressure, 120–150 °C/0.15 mmHg.

Hpyrrole-2-CH=N-R' (R' = (S)-CHMePh, 5; 2,6-xylyl, 6)

A solution of R'NH$_2$ (20 mmol) and Hpyrrole-2-carbaldehyde (20 mmol) in benzene (50 ml) was refluxed for 5 hours. The solvent was distilled off yielding (80%) for R' = (S)-CHMePh a yellow liquid which could be purified by distillation at low pressure, 180 °C/0.15 mmHg. For R' = 2,6-xylyl a white solid was obtained in 65% yield.

The Complexes

[Zn₂{μ-(R)(S)-1,2-(pyrrole-2-CH=N)₂-cyclohexane}₃]

A solution of anhydrous ZnSO$_4$ (1 mmol) in methanol (20 ml) was added to a solution of 1 (1 mmol) in methanol (20 ml). After 15 min a solution of KOH (2 mmol in methanol (30 ml) was added to the reaction mixture which then was stirred for 30 min. The solvent was evaporated off and the residue was dissolved in CH$_2$Cl$_2$ and filtered. The filtrate was concentrated by evaporating the solvent to dryness. The white solid was washed with diethyl ether (3 × 10 ml) yielding pure Zn$_2$(1)$_2$. *Anal.* Calcd for C$_{16}$H$_{18}$N$_4$Zn: C, 57.93; H, 5.47; N, 16.89. Found: C, 57.65; H, 5.54; N, 16.71%.

[Zn₂{μ-1,2-(pyrrole-2-CH=N)₂-ethane}₂]

The preparation of Zn$_2$(2)$_2$ proceeds *via* the method described for Zn$_2$(1)$_2$. The white solid product was recrystallized from methanol. *Anal.* Calcd. for C$_{12}$H$_{12}$N$_4$Zn: C, 51.92; H, 4.36; N, 20.18. Found: C, 51.80; H, 4.59; N, 20.08%.

[Zn(pyrrole-2-CH=N-R')₂] (R' = t-Bu; i-Pr; (S)-CHMePh; 2,6-xylyl)

A solution of anhydrous ZnSO$_4$ (1 mmol) in methanol (20 ml) was added to a solution of H-pyrrole-2-CH=N-R' (2 mmol) in methanol (20 ml). After 15 min a solution of KOH (2 mmol) in methanol (30 ml) was added. The subsequent procedure to obtain the complexes was similar to that described for Zn$_2$(1)$_2$. The complexes were washed with pentane (3 × 10 ml). The solids, with R' = t-Bu, i-Pr and (S)-CHMePh, have a light brown colour while the complex with R' = 2,6-xylyl is coloured deep yellow. *Anal.* Calcd. for C$_{18}$H$_{26}$N$_4$Zn (R' = t-Bu): C, 59.43; H, 7.20; N, 15.40. Found: C, 59.41; H, 7.24; N, 15.46. Calcd for C$_{16}$H$_{24}$N$_4$Zn (R' = i-Pr):

TABLE I. Field Desorption Mass Data[a] of $Zn_2(N_2'N_2)_2$ and $Zn(N'N)_2$ Complexes.

Compound	M/Z, I_{rel} found (calc.)[b]		
$Zn_2(N_2'N_2)_2$; R			
$Zn_2(1)_2$; (R)(S)-1,2-cyclohexane	660,60(81);	661,35(32);	662,100(98);
	663,46(51);	664,68(100);	665,45(44);
	666,35(48);	667,17(21);	668,22(18);
	669,3(6).		
$Zn_2(2)_2$; 1,2-ethane	552,68(84);	553,21(26);	554.86(99);
	555,50(44);	556,100(100);	557,36(37);
	558,33(46);	559,13(18);	560,8(17);
	561,2(5).		
$Zn(N'N)_2$; R'			
$Zn(3)_2$; t-Bu	362,100(100);	363,20(22);	364,59(59);
	365,21(21);	366,47(41);	367,10(9).
$Zn(4)_2$; i-Pr	334,100(100);	335,19(19);	336,57(59);
	337,18(20);	338,39(41);	339,8(8).
$Zn(5)_2$; (S)-CHMePh	458,100(100);	459,32(31);	460,58(62);
	461,25(27);	462,38(43);	463,20(12).
$Zn(6)_2$; 2,6-xylyl	458,100(100);	459,33(31);	460,57(62);
	461,27(27);	462,37(43);	463,20(12).

[a]Emitter current amounts to 5 mA.   [b]I_{rel}, relative intensities (%).

C, 57.24; H, 6.60; N, 16.69. Found: C, 57.27; H, 6.58; N, 16.64. Calcd for $C_{26}H_{26}N_4Zn$ (R' = (S)-CHMePh): C, 67.90; H, 5.70; N, 12.18. Found: C, 67.90; H, 5.69; N, 12.18. Calcd for $C_{26}H_{26}N_4Zn$ (R' = 2,6-xylyl): C, 67.90; H, 5.70; N, 12.18. Found: C, 67.66; H, 5.71; N, 12.19%.

Physical Measurements

Field desorption mass spectra were obtained with a Varian MAT 711 double focussing mass spectrometer with a combined EI/FI/FD ion source and coupled to a spectro-system MAT 100 data acquisition unit, as described in ref. 5. The samples were loaded onto the emitter with the dipping technique [6] (F.D. mass data of the complexes have been listed in Table I).

^1H NMR spectra of both the pure ligands and their zinc(II) complexes were recorded on a Bruker WM 250 spectrometer with tetramethylsilane (TMS) as external reference (for data see Table II).

Molecular weights of the [Zn(pyrrole-2-CH=N-R')$_2$] complexes in chloroform solution were measured with a Hewlett-Packard vapour pressure osmometer Model 320B (for data see Table III). This apparatus does not allow measurements to be performed under a nitrogen atmosphere.

Results

$Zn_2(N_2'N_2)_2$ Complexes

The zinc(II) complexes, $Zn_2(1)_2$ and $Zn_2(2)_2$, with the dianionic $(N_2'N_2)^{2-}$ ligands [(pyrrole-2-CH=N)$_2$-R]$^{2-}$ R = (R)(S)-1,2-cyclohexane (1) or

1,2-ethane (2), were synthesized by reacting Zn-SO$_4$ and $H_2N_2'N_2$ in a 1/1 ratio with two equivalents of KOH in methanol. The analytical data are in agreement with Zn(II)-to-$(N_2'N_2)^{2-}$ ratio of 1/1. The field-desorption mass spectra showed intense peaks at m/z values corresponding to those calculated for dinuclear $Zn_2(N_2'N_2)_2$ species (see Fig. 2) with no fragmentation patterns. The neutral complexes have good solubilities in CH_2Cl_2 and $CHCl_3$.

The ^1H NMR spectrum of $Zn_2(1)_2$, containing the (R)(S)-1,2-cyclohexanediyl bridging groups, showed two pyrrole-2-imine resonance patterns at 294 K in $CDCl_3$ (see Fig. 3). Based on $^1H-^1H$ decoupling experiments two separate sets of pyrrole ^1H resonances (denoted as A and B, see Table II) were assigned. However, it was not possible by a NOE difference experiment to assign the two imine-H resonances at δ 8.07 and δ 6.90 to either the A or the B pyrrole-H patterns. Apparently the distances between the imine-H atoms and the respective pyrrole-H(3) atoms are too large and therefore no
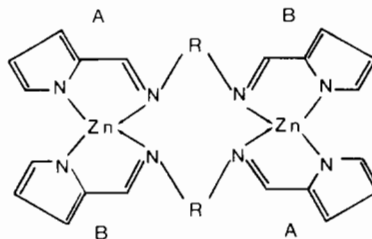

Fig. 2. Schematic representation of the $Zn_2(N_2'N_2)_2$ complexes; $Zn_2(1)_2$, R = (R)(S)-1,2-cyclohexane; $Zn_2(2)_2$, R = 1,2-ethane.

TABLE II. ^{1}H NMR Data[a] of the Neutral $H_2N_2'N_2$ and $HN'N$ Ligands and the Neutral $Zn_2(N_2'N_2)_2$ and $Zn(N'N)_2$ Complexes.

Compound		δ (ppm)					
		H(im)	H-3	H-5	H-4	NC–H	NCC–H
(Hpyrrole-CH=N)₂-R							
(R)(S)-1,2-cyclohexane (1)		7.99s	6.80d	6.41d	6.18dd	3.34m	
1,2-ethane[b] (2)		8.08s	6.97d	6.60d	6.20dd	3.78s	
Zn₂(N₂'N₂)₂							
Zn₂(1)₂	A	8.07s	7.01d	6.73d	6.29dd	3.50m	
	B	6.90s	6.95d	6.54d	6.32dd	3.71m	
Zn₂(2)₂		7.46s	7.07d	6.76d	6.44dd	3.51m	
Hpyrrole-2-CH=N-R'							
t-Bu (3)		8.08s	6.81d	6.45d	6.20dd		1.25s
i-Pr (4)		8.22s	6.93d	6.58d	6.31dd	3.55se	1.32d
(S)-CHMePh (5)		8.15s	7.18d	6.52d	6.19dd	4.50q	1.56d
2,6-xylyl (6)		7.93s	6.57d	6.28d	6.12dd		2.17s
Zn(N'N)₂[c]							
Zn(3)₂		8.16s	7.07d	6.78d	6.39dd		1.22s
Zn(4)₂		8.19s	7.11d	6.84d	6.44dd	3.76se	1.11d
							1.14d
Zn(5)₂[d]	55%	8.20s				4.75q	1.56d
	45%	7.99s				4.34q	1.25d
Zn(6)₂		7.85s	7.31d	6.92d	6.51dd		2.15s
							1.42s

[a]In $CDCl_3$ at room temperature (see Experimental). s = singlet, d = doublet, dd = doublet of doublets, q = quartet, se = septet and m = multiplet.   [b]In methanol-d_4 at room temperature.   [c]In $CDCl_3$ at 213 K.   [d]H-3, H-4 and H-5 resonances could not be assigned with certainty.
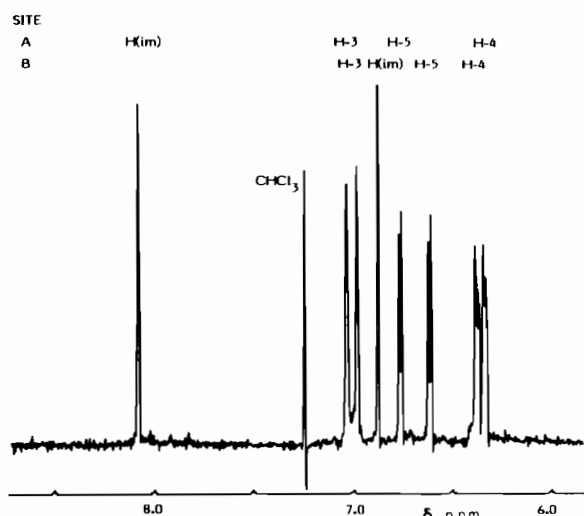

Fig. 3. Part of the ^{1}H NMR spectrum (250 MHz) of Zn_2-(1)₂ in $CDCl_3$ at room temperature.

NOE is generated on the pyrrole-H(3) resonance when irradiating the corresponding imine-H signal.

Compared to the imine-H resonance of the free ligand 1 (δ 7.99) the imine-H resonance at δ 6.90 in $Zn_2(1)_2$ has undergone a large upfield shift of 1.09

ppm while the imine-H resonance at δ 8.07 in the spectrum of the complex has shifted downfield by 0.08 ppm. The pyrrole-H resonances of both the A and the B sites have undergone a downfield shift compared with those in the spectrum of the free ligand.

The ^{1}H NMR spectrum of $Zn_2(2)_2$, which has the 1,2-ethanediyl bridging groups, showed only one pyrrole-imine pattern in $CDCl_3$ from 213 K to 294 K. The 1,2-ethanediyl-H atoms appeared as an AA'BB' resonance pattern. Also in this dinuclear Zn(II) complex a large upfield shift of the imine-H resonance (Δδ 0.62) and a small downfield shift of the pyrrole-H resonances, relative to the free ligand 2, were observed.

$Zn(N'N)_2$ Complexes

The zinc(II) complexes with the bidentate anionic $(N'N)^-$ ligands [pyrrole-2-CH=N-R']⁻ (R' = t-Bu, 3; i-Pr, 4; (S)-CHMePh, 5; 2,6-xylyl, 6) were prepared in methanol by reacting $ZnSO_4$ and the HN'N ligands in a 1/2 ratio with two equivalents of KOH. The analytical data are in good agreement with complexes having a 1/2 zinc(II) to $(N'N)^-$ ratio. This ratio was confirmed by the field-desorption mass spectroscopic data (see Table I), which show patterns with M/Z

TABLE III. Vapour Pressure Osmometric Data of $Zn(pyrrole-2-CH=N-R')_2$ in $CHCl_3$.

Complexes; R'	[C]	M (calc.)	M (found)	Δ(%)[a]
$Zn(3)_2$; t-Bu	0.032	363.8	290.3	−20.2
	0.074		355.2	−2.4
$Zn(4)_2$; i-Pr	0.029	335.8	287.4	−14.4
	0.070		333.7	−0.6
$Zn(5)_2$; (S)-CHMePh	0.033	459.9	354.8	−22.9
	0.073		409.4	−11.0
$Zn(6)_2$; 2,6-xylyl	0.039	459.9	308.2	−33.0
	0.054		344.1	−25.2

[a]The instrumental error will be about 5%.

values corresponding to those calculated for monomeric $Zn(N'N)_2$ species. These neutral complexes not only dissolve well in CH_2Cl_2 and $CHCl_3$ but also in apolar solvents such as benzene and toluene.

Molecular weights of the $Zn(N'N)_2$ complexes in solution were obtained by vapour pressure osmometric measurements in $CHCl_3$, which gave the expected values for the monomeric complexes $Zn(3)_2$ (R' = t-Bu) (0.074 M) and $Zn(4)_2$ (R' = i-Pr) (0.070 M) (see Table III). It must be noted that the data obtained for lower concentrations of $Zn(3)_2$ (0.032 M) and $Zn(4)_2$ (0.029 M) and for the complexes $Zn(5)_2$ (R' = (S)-CHMePh) and $Zn(6)_2$ (R' = 2,6-xylyl) showed large deviations from the calculated monomeric values. This is probably due to the occurrence of hydrolyses of Zn-N(pyrrole) bonds followed by complete metal-ligand dissociation (see Experimental).

The complex $Zn(pyrrole-2-CH=N-t-Bu)_2$ has already been prepared by Holm and co-workers [2] and some crystallographic data, such as space group (Pbcn) and cell constants have been published [7]. In order to investigate the coordination properties of the pyrrole-2-CH=N-moieties to zinc(II) in more detail we solved the X-ray structure of complex 3 (see ref. 8). Relevant for the present study is the PLUTO drawing of the molecule (Fig. 4), which shows that the zinc(II) centre is coordinated by four nitrogen atoms and that it has a distorted tetrahedral geometry. This distortion is caused by the acute bite angles $(84.1(1)°)$ of the bidentate (pyrrole-2-CH=N-t-Bu)⁻ ligands and the different Zn−N(imine) and Zn−N(pyrrole) distances. The Zn−N distances of 2.067(2) Å and 1.975(2) Å are in the range normally found for donative N−Zn and covalent N−Zn distances respectively [1, 9, 10]. The pyrrole ring atoms, the C=N atoms of each ligand as well as the Zn(II) centre (*i.e.*, the five membered chelate ring) are all in one plane. The two planes then formed by the two ligands and the metal centre are related by a two fold axis with a mutual angle of $89.2(1)°$.

¹H NMR data of the complexes dissolved in $CDCl_3$ showed that on complexation of the (N'N)⁻ mono-
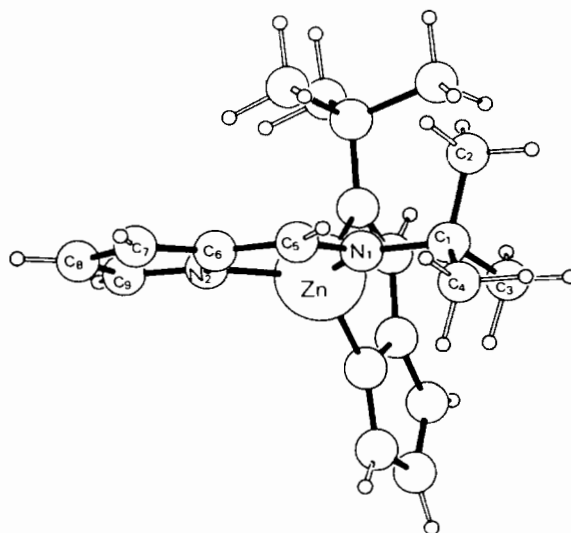

Fig. 4. PLUTO drawing of $Zn(3)_2$ (R' = t-Bu).

anionic ligands to zinc(II) the pyrrole-H· resonances have shifted downfield and the =N−C−C−*H* resonances of the respective R' substituents upfield. Only small chemical shift changes are observed for the imine-H resonances, see Table II. The latter table contains the ¹H NMR data of the complexes in the slow exchange regions.

The ¹H NMR spectra of $Zn(3)_2$ (R' = t-Bu) showed one pattern for the pyrrole-imine-H atoms and a singlet for the H-atoms of the t-Bu groups in the temperature range studied (213–300 K). From these data no conclusions could be drawn either about the coordination properties of the ligands or the geometry of the zinc(II) centre of $Zn(3)_2$ in solution. For this reason we have also prepared the $Zn(N'N)_2$ complexes with ligands having the prochiral i-Pr group as imino-substituent, *i.e.* $Zn(4)_2$, or with ligands having the (S)-CHMePh group containing a chiral C-atom with absolute configuration (S), *i.e.* $Zn(5)_2$.

The ¹H NMR spectrum of $Zn(4)_2$ (R' = i-Pr) showed at low temperature (213 K) one pyrrole-imine-H
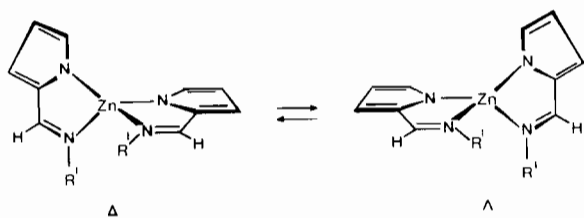
Fig. 5. The two enantiomeric forms of the $Zn(N'N)_2$ complexes.

pattern and two doublets for the isopropylmethyl-H atoms with a very small diastereotopic splitting of 5.8 Hz (250 MHz). In the ^1H NMR spectrum at 213 K of $Zn(5)_2$ ($R' = (S)$-CHMePh) two ligand patterns are observed in a 55/45 intensity ratio. These results are in accordance with a tetrahedral geometry for the zinc(II) centre of the $Zn(N'N)_2$ complexes in solution as has been established for $Zn(3)_2$ in the solid state. The existence of two possible configurations of the Zn(II) centre, either Δ or Λ (see Fig. 5), is reflected in the ^1H NMR patterns found for these complexes. When R' is i-Pr the complex, $Zn(4)_2$, exists in two enantiomeric forms. At low temperatures these enantiomers are stable on the NMR time scale, which renders the methyl groups in the prochiral i-Pr groupings diastereotopic. When R' is the chiral (S)-CHMePh substituent these enantiomers become diastereomers with either $\Delta(S)(S)$ or $\Lambda(S)(S)$ configurations, and they can then be detected separately in the ^1H NMR spectrum.

On increasing the temperature, the spectra (250 MHz) of $Zn(4)_2$ ($R' = $ i-Pr) in $CDCl_3$ showed a coalescence of the two isopropyl-methyl doublet resonances with $\Delta\nu$ 5.8 Hz to one doublet at 260 K. This observation clearly reveals that in solution at higher temperatures a $\Delta \rightleftarrows \Lambda$ inversion process between the enantiomeric forms of the $Zn(N'N)_2$ complexes is taking place, and is then fast on the NMR time scale (e.g. for $R' = $ i-Pr above 260 K).

To investigate whether this inversion at the Zn(II) centre proceeds via an intra or intermolecular process (see Discussion) we have prepared a mixture of complex $Zn(3)_2$ ($R' = $ t-Bu, 0.086 M) and $Zn(4)_2$ ($R' = $ i-Pr, 0.090 M). The ^1H NMR spectra of this sample showed across the whole temperature range (213–300 K) sharp, separate resonance patterns which belong to pure $Zn(3)_2$ and $Zn(4)_2$. Accordingly no mixed complexes are formed, indicating that no intermolecular ligand exchange is taking place when only the pure $Zn(N'N)_2$ complexes are present in solution. We therefore may conclude that the $\Delta \rightleftarrows \Lambda$ inversion is primarily an intramolecular process.

In solutions of $Zn(5)_2$ ($R' = (S)$-CHMePh) a similar inversion process as found for $Zn(4)_2$, but now occurring between the two diastereoisomers $\Delta(S)(S)$ and $\Lambda(S)(S)$, is observed. The fact that the ^1H NMR spectrum at room temperature of $Zn(5)_2$ contains

only one pyrrole-2-CH=N-(S)-CHMePh pattern points out that at this temperature the inversion process is fast on the NMR time scale.

The ^1H NMR spectrum at 213 K of complex $Zn(6)_2$ ($R' = $ 2,6-xylyl) showed one pattern for the H-atoms of the two ligands, except for those of the ortho-methyl groups which appeared as two singlets. If this complex has likewise a tetrahedral geometry this result indicates that rotation of the 2,6-xylyl groups around the $(C=)N-C$ bonds must be hindered at this temperature. The observation that in the ^1H NMR spectrum at room temperature these two methyl resonances have coalesced to one singlet supports this idea. Rotation of the 2,6-xylyl groups then has become fast on the NMR time scale. However, an exchange process involving inversion of configuration of the metal centre ($\Delta \rightleftarrows \Lambda$) as described for $Zn(4)_2$ may likewise be responsible for the observed coalescence. Unfortunately it has not been possible to discriminate between these two processes, i.e, aryl rotation and inversion of configuration at Zn(II), from the available ^1H NMR data of $Zn(6)_2$.

Discussion

$Zn_2(N'_2N_2)_2$

The F.D.-mass data provide direct evidence for the dimeric nature of the zinc(II) complexes, $Zn_2(1)_2$ and $Zn_2(2)_2$, containing the $(N'_2N_2)^{2-}$ dianionic ligands [(pyrrole-2-CH=N)$_2$-R]$^{2-}$ ($R = (R)(S)$-1,2-cyclohexane or 1,2-ethane).

The appearance of two pyrrole-2-imine patterns in the ^1H NMR spectrum of $Zn_2(1)_2$ with the $(R)(S)$-1,2-cyclohexanediyl bridging groups is a strong indication that these neutral zinc(II) complexes have helix type dimeric structures in solution similar to those found for the dications formed in the reactions of [M(O$_3$SCF$_3$)] [M = Ag(I) or Cu(I)] with the neutral N'_2N_2 and N_2S_2 donor ligands $(R)(S)$-1,2-(X-2-CH=N)$_2$-cyclohexane (X = pyridine [11, 12] or thiophene [13]). The PLUTO drawing (see Fig. 6) of the structure in the solid of one of these dications, i.e. [Ag$_2$(N'$_2$N$_2$)$_2$]$^{2+}$, illustrates the di-bidentate bonding mode of these neutral N'_2N_2 ligands, as well as the helix type structure of the dication. The silver(I) centres in the dication have distorted tetrahedral geometries and are coordinated by alternating short Ag—N(imine) (A), Ag—N(pyridine) (B) and long Ag—N(imine) (B) and Ag—N(pyridine) (A) distances.

From ^1H, ^{15}N and ^{109}Ag NMR results it was concluded that the silver(I) complex has a structure in solution the same as has been found in the solid, i.e. both metal centres have either Δ or Λ configurations and the $(R)(S)$-cyclohexanediyl groups are positioned, in an endo situation, such that the
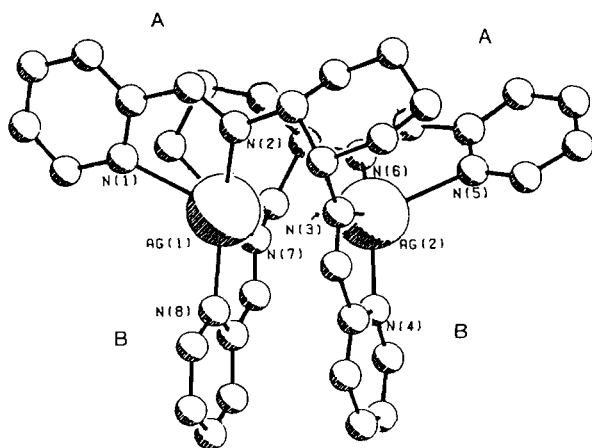
Fig. 6. PLUTO drawing of the $[Ag_2(N_2'N_2)_2]^{2+}$ dication with the $N_2'N_2$ ligands $(R)(S)$-1,2-(py-2-CH=N)$_2$-cyclohexane. Hydrogen atoms are omitted for clarity.

C-atoms with opposite configurations are facing each other [12]. The structure of the complex is then denoted as endo-$\Delta_{RS}^{SR}\Delta$ (this notation represents the structure in Fig. 6) or its enantiomer endo-$\Lambda_{SR}^{RS}\Lambda$. Based on this structure the very different ^{1}H NMR chemical shifts found for the two types of (pyridine-2-imine)-H-atoms could be rationalized. The structure shows that in contrast to the well-separated pyridine rings (denoted as A in Fig. 6) the other two pyridine rings B are parallel-positioned. The ^{1}H-atoms of the latter pyridine rings therefore experience a ring current effect resulting in the characteristic shifts in the ^{1}H NMR spectrum.

When the neutral zinc(II) complex $Zn_2(1)_2$ has the endo-$\Delta_{RS}^{SR}\Delta$ structure in solution the large upfield shift of the imine-H resonance at $\delta 6.90$ and the relative upfield position of the pyrrole-H-3 and H-5 signals of site B (see Table II) can be ascribed as arising from a similar ring current effect that results from parallel positioned pyrrole-2-imine moieties. Therefore, we assume that the imine-H resonance at $\delta 6.90$ and the pyrrole-H resonances (denoted as B), are representing the H-atoms of the isochronous parallel pyrrole-2-imine moieties.

A study of molecular models showed that the Zn_2-$(2)_2$ complex having the 1,2-ethanediyl bridging groups has the same structure as $Zn_2(1)_2$ with two well-separated pyrrole rings (A) and two parallel-positioned pyrrole-imine moieties (B). In contrast to the observation of two pyrrole-imine-H patterns in the ^{1}H NMR spectrum of $Zn_2(1)_2$, only one such pattern is present in the spectra of $Zn_2(2)_2$ from 213 K to 294 K. Apparently a H(A)–H(B) exchange process is taking place which is already fast at 213 K. This process has also been observed for the $[M_2$-$(N_2'N_2)_2]^{2+}$ dications [M = Ag(I) or Cu(I)] having 1,2-ethanediyl bridging groups. The observed H(A)–H(B) exchange is caused by a fluxional movement

which occurs between identical structural conformations (see Fig. 5 in ref. 12). Further support for this view is provided by the observation that the chemical shift of the imine-H resonance in $Zn_2(2)_2$ is lying between the chemical shift positions of the imine-H(A) and imine-H(B) in the ^{1}H NMR spectrum of $Zn_2(1)_2$.

In the case of $Zn_2(1)_2$ such conformational movement would take place between different, diastereomeric, structures and because of the difference in stabilities of these diastereomers this fluxional process does not occur.

In our recent study of the dynamic solution behaviour of the $[Ag_2(N_2'N_2)_2]^{2+}$ dications heteronuclear coupling information, $i.e.$ $^3J(^1H-^{107,109}Ag)$, was of crucial importance [12]. Intermolecular processes, which were monitored by following the disappearance of this coupling as a function of the temperature and the concentration of added [Ag-(O_3SCF_3)], induced an intramolecular process involving inversion of both metal centres ($\Delta\Delta\rightleftarrows\Lambda\Lambda$). This process was observed in the ^{1}H NMR spectra of the $[Ag_2(N_2'N_2)_2]^{2+}$ dication shown in Fig. 6 as imine-H(A)–H(B) exchange. It could be concluded that the mechanism for this imine-H(A)–H(B) exchange which is induced by intermolecular Ag$^+$ exchange involved initial Ag–N(pyridine) bond dissociation, $i.e.$ cleavage of the interaction between one of the outer N-sites of the $N_2'N_2$ ligand and the Ag(I) centre.

In contrast, for $Zn_2(1)_2$ and $Zn_2(2)_2$ direct information concerning the nature of the Zn–N interactions could not be obtained from their ^{1}H NMR spectra. No $^3J(^1H-^{67}Zn)$ (^{67}Zn, I = 5/2, 4.11%) could be observed on the imine-H resonances. An important difference between the $[Ag_2(N_2'N_2)_2]^{2+}$ dication and the neutral dinuclear Zn(II) complexes is the fact that in the latter complexes the $[(pyrrole-2-CH=N)_2R]^{2-}$ ligands are bonded to the Zn(II) centres via covalent Zn–N(pyrrole) bonds. Accordingly the outer two N centres of the (N_2'-$N_2)^{2-}$ ligands are tightly bonded to the Zn(II) centres, thereby blocking the first step of a possible intermolecular exchange process. This is confirmed by the fact that evidence for the occurrence of imine-H(A)–H(B) exchange in $Zn_2(1)_2$ could not be obtained even during the homonuclear decoupling experiments (see Results).

This study shows that the dianionic pyrrole-imine ligands, $(N_2'N_2)^{2-}$ react with Zn(II) to give stable dinuclear zinc complexes in which these ligands are bonded as di-bidentates. $Zn(N_2'N_2)$ complexes are probably not formed, because they would contain three five membered chelate rings which has been proven to be unfavourable [14], and because Zn(II) centres prefer tetrahedral geometries when four coordinate.

The formation of dinuclear species is in contrast with the proposed monomeric $Zn(N_2'N_2)$ structures

for some zinc(II) open chain tetrapyrrole complexes in which the ligand acts as a quadridentate ligand [15]. For the latter complexes no ring closure reactions of the open chain tetrapyrrole were observed to form corrinoid or porphyrinoid macrocycles [16]. It is obvious that the preference for the di-bidentate bonding mode, as we have found in solution for $Zn_2(1)_2$ and $Zn_2(2)_2$, of such $(N'_2N_2)^{2-}$ ligands with Zn(II) will restrict the ring closure reaction.

$Zn(N'N)_2$

The coordination properties of the (pyrrole-2-CH=N-R')$^-$ monoanions in $Zn(3)_2$ (R' = t-Bu) in the solid have been studied in detail by X-ray methods (see Results). The PLUTO drawing clearly shows that the metal centre in $Zn(3)_2$ has a distorted tetrahedral geometry caused by the acute bite angles of the ligands and the difference between the Zn–N-(imine) and Zn–N(pyrrole) distances.

The ^{1}H NMR spectra of $Zn(4)_2$ (R = i-Pr) and Zn-$(5)_2$ (R = (S)-CHMePh) at 213 K clearly reveal that the zinc(II) centres have tetrahedral geometries in solution in which the metal centres have either Δ or Λ configurations. The coalescence of the two doublets of the methyl groups of the prochiral i-Pr substituents in $Zn(4)_2$ to one doublet resonance in the ^{1}H NMR spectrum at 260 K indicates that a $\Delta \rightleftarrows \Lambda$ exchange process is taking place. This process becomes fast on the NMR time scale above the coalescence temperature of 260 K. Holm and co-workers [17] studied exchange processes involving the inversion of configuration of tetrahedrally-coordinated metal centres for zinc(II) and cadmium-(II) complexes with β-aminothionato [(NS)$^-$] ligands by dynamic ^{1}H NMR spectroscopy. They considered various mechanisms for the $\Delta \rightleftarrows \Lambda$ exchange *via* either intramolecular pathways, *e.g. i*, a twist motion generating a planar transition state, *ii*, by rupture of one or more metal–ligand bonds or *via* an intermolecular route. In the latter case the rate determining step of the process could be either metal–ligand bond rupture or formation of a binuclear intermediate.

The ^{1}H NMR data of our $Zn(N'N)_2$ complexes show that the rate of $\Delta \rightleftarrows \Lambda$ exchange is independent of the concentration of pure complex and that scrambling of ligands, *i.e.* formation of a mixed complex, does not occur in the case of a 1/1 molar mixture of the complexes $Zn(3)_2$ and $Zn(4)_2$. This indicates that the covalent Zn–N(pyrrole) bonds are stable on the NMR time scale and the $\Delta \rightleftarrows \Lambda$ inversion process must primarily occur *via* an intramolecular mechanism.

Possible routes involve Zn–N(imine) bond dissociations leading to either three coordinate or even two coordinate Zn intermediates. Reformation of the tetrahedral situation may lead to either inversion or retention of the configuration of the metal centre.

The occurrence of a possible intramolecular pathway *via* a planar transition state is less likely especially in the case of R' is 2,6-xylyl where the methyl groups of the 2,6-xylyl substituents will come in close contact in such an intermediate.

The neutral monomeric zinc(II) complexes with the (N'N)$^-$ ligands reported in this paper are only a selected group of a larger series of $Zn(N'N)_2$ complexes that may be prepared. Different substituents R' can be built into the Hpyrrole-2-CH=N-R' system (*e.g.* alkyl or aryl substituents) and hence zinc(II) complexes may be prepared having specific electronic and/or stereochemical properties.

We are currently investigating whether these zinc-(II) complexes can play a key function in the aldehyde or imine substrate reduction reactions by NADH model systems, like the Hantzsch ester. As a result of the good solubilities of the monomeric complexes in benzene and toluene it is possible to study these reductions in aprotic media. This may provide information concerning the involvement of radical type of mechanisms for these reactions, as has been observed in the reductions of aldehydes, ketones and imines in organozinc chemistry [9, 18].

Conclusions

From the reactions of the dianionic [(pyrrole-2-CH=N)$_2$-R]$^{2-}$ ligands (R = (R)(S)-1,2-cyclohexane or 1,2-ethane) with Zn(II) dimeric $Zn_2(N'_2N_2)_2$ complexes were obtained. The dimeric nature of the complexes in the solid was established by field-desorption mass spectrometry. From a comparison of the ^{1}H NMR results obtained for the silver(I) dications $[Ag_2(N'_2N_2)_2]^{2+}$ (N'$_2$N$_2$ = (py-2-CH=N)$_2$-R; R = (R)(S)-1,2-cyclohexane or 1,2-ethane) and the results found for the neutral $Zn_2(N'_2N_2)_2$ complexes it was concluded that in solution the zinc(II) complexes have structures similar to those of the silver(I) dications. The zinc(II) complexes thus have dimeric structures in solution in which the $(N'_2N_2)^{2-}$ ligands act as di-bidentates. The metal centres have tetrahedral geometries and both have either Δ or Λ configurations. Because of the presence of strong covalent Zn–N(pyrrole) bonds no intramolecular exchange processes were observed in solution of the complex having the (R)(S)-1,2-cyclohexanediyl bridging groups. This complex has a rigid structure in solution. The ^{1}H NMR results of the complex with the 1,2-ethanediyl bridges reveal that at 213 K in CDCl$_3$ a fast conformational movement between two identical structures is taking place. Because of the lack of heteronuclear coupling information, *i.e.* $^3J(^1H-$ $^{67}Zn)$, it was not possible to determine whether intermolecular metal or ligand exchange processes are also taking place in the latter complex.

From the reactions of half the $(N_2' N_2)^{2-}$ ligand system, *i.e.* the reactions of (pyrrole-2-CH=N-R')⁻ ligands [(N'N)⁻] with Zn(II), the neutral monomeric Zn(N'N)$_2$ complexes were obtained. In solution the Zn(II) centres have tetrahedral geometries as established by the ^{1}H NMR results when R' is the prochiral i-Pr or the chiral (*S*)-CHMePh substituent at 213 K in CDCl$_3$. At higher temperatures (above 260 K for R' = i-Pr) an exchange process is observed involving inversion of configuration of the metal centre. Because it is difficult to break the strong covalent Zn—N-(pyrrole) bonds this exchange process will take place *via* an intramolecular pathway.

Acknowledgements

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