Notes

Characterization of a Zinc(II) Complex of a 15-Membered Macrocyclic Ligand in the Solid State and in Solution: *X*-Ray Structure of (6,7,8,13,14,15,16,17,18,19-Decahydro-5*H*-[*e,n*][1,4,8,12]-tetra-azacyclopentadecine)iodozinc(II) Iodide †

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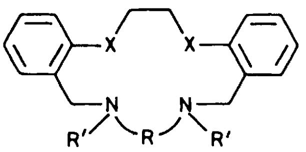
Reaction of the title 15-membered macrocyclic ligand (L^1) with ZnI_2 leads to the isolation of $[Zn(L^1)I][I]$. The *X*-ray structure determination of this complex confirms a square-pyramidal co-ordination geometry for the Zn^{II}, in which the metal is bound by the four nitrogens of the macrocycle and has one axial iodine ligand. N.m.r. spectroscopic measurements confirm the 1 : 1 zinc to ligand stoicheiometry in solution and indicate that the complex undergoes slow chemical exchange at ambient temperature. The complex crystallises in monoclinic space group $P2_1/c$ with a = 8.279(3), b = 18.211(6), c = 14.723(4) Å, and β = 99.21(4)°. The structure was refined to R = 0.033 for 2 597 reflections.

Recent work [1] in these laboratories has been directed towards an examination of the interaction between X_2N_2-donor macrocycles of type (1) (X = O, S, or NH) and a variety of first-row transition and non-transition metal ions. A study of kinetic, thermodynamic, and stereochemical aspects of the complexes has been directed at assessing the potential of these ligand systems for selective chelation. *X*-Ray structural determinations have necessarily played a major role in the investigations so far, allowing variations in stability constants to be interpreted in terms of the structural features of the complexes.

We report now the structure of the new complex $[Zn(L^1)I][I]$ as well as n.m.r. spectroscopic evidence for the nature of the species in solution.



(1)

L^1 : X = NH, R = $-(CH_2)_3-$, R' = H
L^2 : X = O, R = $-(CH_2)_3-$, R' = Me

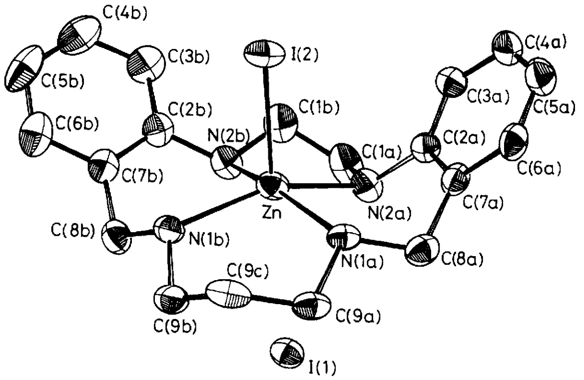


Figure 1. The molecular structure of $[Zn(L^1)I][I]$

Results and Discussion

Mixing stoicheiometric quantities of L^1 ‡ with ZnI_2 in methanol gave crystals of $[Zn(L^1)I][I]$ suitable for diffraction studies. Figure 1 is a view of the complex with hydrogen atoms omitted for clarity. The cation has a slightly distorted square-pyramidal geometry with the base of the pyramid being defined by the four nitrogen atoms of the macrocycle. These four atoms are coplanar to within 0.1 Å. The metal atom is displaced 0.41 Å from the N_4-donor plane towards the iodine I(2) in the axial (fifth) site. The ionic iodide I(1) is located diametrically opposite I(2) on the other side of the zinc atom at a distance of 3.6 Å from it [I(2)–Zn ··· I(1) 178°]. The Zn–N bond lengths appear unremarkable [2] and fall in the range 2.09—2.22 Å. The Zn–I(2) bond length is 2.662(1) Å, which is close to the sum of the covalent radius of I and the dsp^3 radius of Zn^{II} (2.63 Å).[3] The co-ordinated macrocycle has both phenyl rings orientated on the same side of the molecule as the axial iodine.

Evidence that the displacement of the metal ion from the macrocycle cavity results from interaction with the axial iodine (and is not due to mismatch between the diameter of the ' hole ' and the radius of the zinc ion) is provided by the

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† *Supplementary data available* (No. SUP 23624, 27 pp.): complete thermal parameters, atomic co-ordinates, bond lengths and angles, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

‡ The ligand was prepared (C. W. G. Ansell and P. A. Tasker, unpublished work) by the $LiAlH_4$ reduction of the precursor di-imine (see P. G. Owston, R. Peters, E. Ramsammy, P. A. Tasker, and J. Trotter, *J. Chem. Soc., Chem. Commun.*, 1980, 1218).

partial * structure determination[4] of $[Zn(L^1)(ClO_4)_2]$. The results of this study show that the metal ion lies approximately in the best plane through the N_4-donor set of the macrocycle and to be six co-ordinate overall, with perchlorates occupying the axial sites.

It is of interest to compare the geometry of $[Zn(L^1)I][I]$ with that of the ZnI_2 complex[5] of the closely related macrocycle L^2. The substitution of O for N in two of the donor sites has a profound effect on the configuration of the system. The macrocycle adopts a folded configuration with the Zn atom outside the macrocyclic cavity. Both iodine atoms and both nitrogen atoms co-ordinate to the zinc while the ether oxygens remain unco-ordinated. The co-ordination geometry is distorted tetrahedral. The different structural behaviour observed for the two systems is undoubtedly a reflection of the lower affinity of ether donors relative to saturated nitrogen donors for this ion.

The complexation of L^1 by Zn^{II} in $[^2H_6]$dimethyl sulphoxide has been investigated by ^1H and ^{13}C n.m.r. spectroscopy. Incremental addition of ZnI_2 to a solution of the macrocycle resulted in a decrease in the intensity of the uncomplexed ligand peaks and a concomitant rise of new peaks corresponding to the co-ordinated ligand. Both sets of spectra clearly indicate slow ligand exchange at ambient temperature (27 °C) with respect to the n.m.r. time-scales. However, the ^{13}C spectrum of the solution containing a metal : ligand ratio of 1 : 2 at 170 °C showed virtual coalescence of the individual free and complexed ligand peaks observed at 27 °C. Hence, at the higher temperature, ligand exchange has become fast on the n.m.r. time-scale. Such behaviour has been observed[6,7] in other macrocyclic systems. The ^1H and ^{13}C spectral data obtained in the present study also confirm 1 : 1 complexation since no further change in the respective spectra occurred after this ratio of zinc to ligand was exceeded.

The greater chemical shift differences in the carbon spectra resulted in them being easier to study than the proton spectra, for which extensive signal overlap occurred. At ambient temperature the ^{13}C spectrum corresponding to the complexed macrocycle contains approximately twice the number of peaks expected for a 1 : 1 complex in which the macrocycle is co-ordinated in a symmetrical environment (Figure 2). The additional spectral complexity could result from either co-ordination of the ligand in a conformationally inert manner such that the two halves of the macrocycle are not equivalent, or alternatively from the presence of (at least) two distinct conformers in solution which do not undergo fast exchange at 27 °C with respect to the n.m.r. time-scale. The large observed differences between peak heights for resonances in similar regions of the spectrum are more consistent with the latter situation, as the former would be expected to yield peaks of near equal intensity from corresponding atoms in each half of the molecule. However, the two possibilities are not mutually exclusive.

The effect of temperature on the ^{13}C and ^1H n.m.r. spectra of the co-ordinated ligand in the presence of excess of ZnI_2 was investigated in the range 27—170 °C. Line broadening followed by coalescence of certain peaks was evident in both spectra as the temperature increased. Thus at higher temperatures the system changes from slow to fast exchange, with the final high-temperature spectrum consisting of a simple pattern indicating complete averaging of corresponding signals arising from the co-ordinated ligand. A selection of ^{13}C spectra are included in Figure 2. A complicated line-broadening temperature profile was especially evident in the proton spectra, indicating the occurrence of more than one dynamic process. Because of this complexity, a detailed analysis of the spectral changes was not attempted.

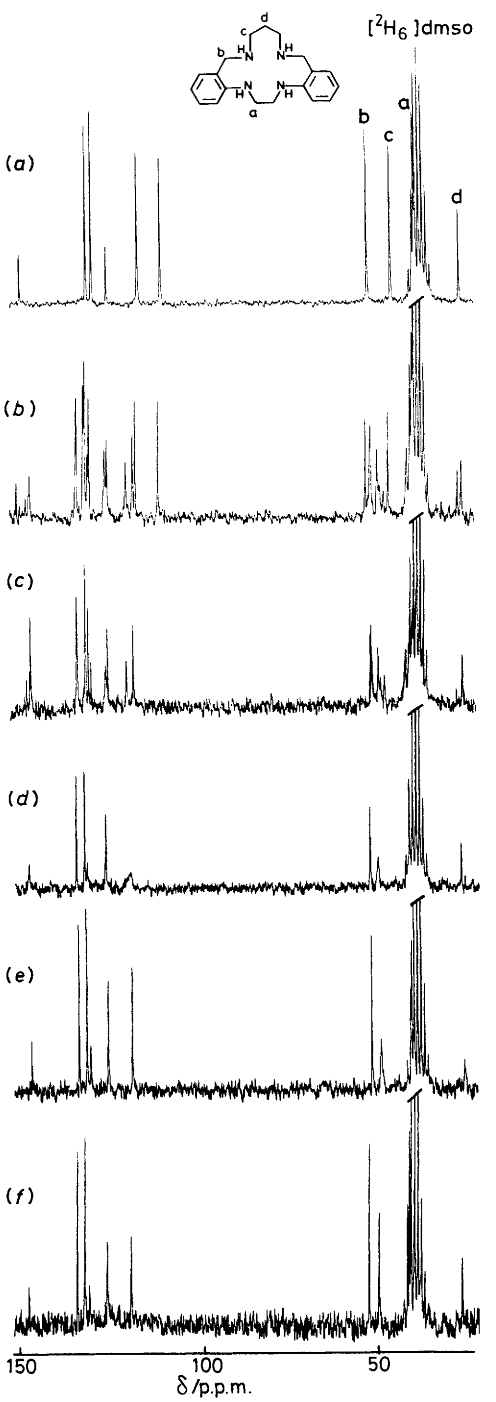

Figure 2. Proton-decoupled ^{13}C n.m.r. (22.49 MHz) spectra showing the effects of addition of ZnI_2 to macrocycle L^1 in $[^2H_6]$dimethyl sulphoxide ($[^2H_6]$dmso) under various conditions: (*a*) 27 °C, $[L^1] = 0.06$ mol dm^{-3}; (*b*) 27 °C, $[Zn^{2+}] : [L^1] = 0.66$; (*c*) 27 °C, $[Zn^{2+}] : [L^1] = 3.20$; (*d*) 85 °C, $[Zn^{2+}] : [L^1] = 3.20$; (*e*) 140 °C, $[Zn^{2+}] : [L^1] = 3.20$; (*f*) 170 °C, $[Zn^{2+}] : [L^1] = 3.20$

The slow chemical exchange observed for this system at lower temperature contrasts with the behaviour in $[^2H_6]$-dimethyl sulphoxide of the corresponding N_2O_2 system $[Zn(L^2)I_2]$, in which the ether oxygens do not co-ordinate.

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* The poor quality of the data and pseudo-symmetry between the two molecules in the asymmetric unit precluded satisfactory structure determination of this compound.

Table 1. Fractional atomic co-ordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn	0.013 91(9)	0.332 21(4)	0.366 14(6)	C(4a)	−0.418 7(10)	0.513 7(5)	0.237 2(5)
I(1)	0.270 93(6)	0.289 50(3)	0.198 15(3)	C(3a)	−0.354 4(9)	0.445 8(4)	0.222 2(5)
I(2)	−0.184 69(6)	0.365 66(3)	0.485 46(4)	C(2a)	−0.185 1(8)	0.437 0(4)	0.238 3(5)
N(1a)	0.137 9(6)	0.435 4(3)	0.376 2(4)	C(1a)	−0.199 8(10)	0.307 4(4)	0.176 9(6)
N(2a)	−0.104 9(7)	0.367 6(3)	0.227 6(4)	C(1b)	−0.245 3(10)	0.251 6(5)	0.239 4(6)
N(1b)	0.185 7(6)	0.268 8(3)	0.451 5(4)	C(2b)	−0.117 1(9)	0.175 8(4)	0.370 1(5)
N(2b)	−0.096 7(7)	0.230 0(3)	0.302 8(4)	C(3b)	−0.268 8(11)	0.148 3(5)	0.379 1(6)
C(9c)	0.358 0(9)	0.380 5(4)	0.490 8(5)	C(4b)	−0.283 5(13)	0.096 0(6)	0.445 1(7)
C(9a)	0.318 1(8)	0.431 6(4)	0.408 9(5)	C(5b)	−0.150 1(15)	0.072 7(5)	0.503 3(7)
C(8a)	0.100 0(8)	0.484 8(4)	0.295 8(5)	C(6b)	0.004 0(13)	0.102 4(4)	0.497 5(6)
C(7a)	−0.083 1(8)	0.496 4(4)	0.270 9(5)	C(7b)	0.023 1(10)	0.154 7(4)	0.431 4(5)
C(6a)	−0.156 6(10)	0.563 3(4)	0.284 0(5)	C(8b)	0.186 6(9)	0.189 4(4)	0.429 9(5)
C(5a)	−0.322 5(10)	0.572 8(4)	0.266 5(6)	C(9b)	0.355 6(8)	0.299 2(4)	0.467 6(5)

Table 2. Selected bond lengths (Å) and angles (°)

Zn–I(2)	2.662(1)	N(1b)–C(8b)	1.480(9)	Zn · · · I(1)	3.597(1)	C(7b)–C(8b)	1.497(10)
Zn–N(1a)	2.135(5)	C(2b)–C(7b)	1.406(10)	Zn–N(2a)	2.214(6)	N(2b)–C(2b)	1.428(9)
Zn–N(1b)	2.089(5)	N(2b)–C(1b)	1.474(9)	Zn–N(2b)	2.213(6)	C(1a)–C(1b)	1.460(11)
N(1a)–C(9a)	1.494(8)	C(1a)–N(2a)	1.479(9)	C(9a)–C(9c)	1.516(10)	N(2a)–C(2a)	1.447(8)
C(9c)–C(9b)	1.518(10)	C(7a)–C(8a)	1.516(9)	N(1b)–C(9b)	1.495(8)	N(1a)–C(8a)	1.480(9)

I(2)–Zn–I(1)	177.9(1)	C(2a)–N(2a)–Zn	107.3(4)	N(1b)–Zn–N(2a)	151.0(2)
N(1a)–Zn–I(2)	95.4(1)	C(1a)–N(2a)–C(2a)	119.1(6)	N(2b)–Zn–I(2)	102.3(2)
N(2a)–Zn–I(2)	108.1(2)	C(9b)–N(1b)–Zn	115.0(4)	N(2b)–Zn–N(2a)	76.3(2)
N(1b)–Zn–I(1)	82.7(2)	C(1b)–N(2b)–Zn	106.8(5)	C(9a)–N(1a)–Zn	115.2(4)
N(1b)–Zn–N(1a)	99.9(2)	C(2b)–N(2b)–C(1b)	116.4(6)	C(8a)–N(1a)–C(9a)	111.0(5)
N(2b)–Zn–I(1)	77.2(2)	N(1a)–Zn–I(1)	84.7(1)	C(1a)–N(2a)–Zn	111.8(5)
N(2b)–Zn–N(1a)	158.6(2)	N(2a)–Zn–I(1)	69.7(2)	C(8b)–N(1b)–Zn	115.9(4)
N(2b)–Zn–N(1b)	89.1(2)	N(2a)–Zn–N(1a)	86.9(2)	C(9b)–N(1b)–C(8b)	111.1(5)
C(8a)–N(1a)–Zn	116.2(4)	N(1b)–Zn–I(2)	99.4(2)	C(2b)–N(2b)–Zn	112.1(4)

This latter system undergoes fast exchange at ambient temperature. The observed difference in behaviour of these systems undoubtedly reflects the co-ordination of all four donors in the N_4 system, which will thus be liable to enhancement of kinetic inertness due to the ' macrocyclic effect '.[8]

Experimental

The *X*-ray data were collected as previously described.[9] Crystals of the title complex were grown from methanol containing a 1 : 1 ratio of ZnI_2 and L^1. The two iodine atoms were found from a Patterson map and all remaining non-hydrogen atoms from subsequent difference maps. All non-hydrogen atoms were refined anisotropically. Hydrogens were included in calculated positions 0.95 Å from the parent atom. Tables 1 and 2 list positional parameters and selected bond lengths and angles. All calculations were performed using SHELX.[10]

Crystal data. $[Zn(L^1)I][I]$, Monoclinic, space group $P2_1/c$, $a = 8.279(3)$, $b = 18.211(6)$, $c = 14.723(4)$ Å, $\beta = 99.21(4)°$, $Z = 4$, $U = 2\,191.1$ Å^3, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 28.6$ cm^{-1}, $F(000) = 1\,208$.

The structure was refined to $R = 0.033$, $R' [= \Sigma w^{\frac{1}{2}} \Delta/\Sigma w^{\frac{1}{2}}|F_o|$, with weights $w = 1/|\sigma^2(F)|] = 0.033$, for 2 597 reflections $[F > 6\sigma(F)]$ obtained on a crystal of dimensions 0.20 × 0.25 × 0.18 mm. The cell constants for $[Zn(L^1)(ClO_4)_2]$ are: monoclinic, space group $P2_1/n$, $a = 8.598(4)$, $b = 17.666(7)$, $c = 15.439(5)$ Å, and $\beta = 91.91(6)°$.

N.m.r. titrations were performed by adding known increments of solid ZnI_2 to an n.m.r. tube containing a known weight of ligand dissolved in $[^2H_6]$dimethyl sulphoxide. A JEOL-FX90Q spectrometer was used. The experiments were terminated when the Zn : L^1 ratio reached 3 : 1. A total of ten separate additions were made in each of the ^1H and ^{13}C runs. No evidence was obtained for the formation of complexes having a M : L ratio other than 1 : 1. In the variable-temperature studies, spectra were obtained at six temperatures in the range 27—170 °C. At the end of the experiment the solution was cooled to 27 °C and rerun to confirm that no decomposition had occurred.

Acknowledgements

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