Comparison of the Structure and Dynamic Properties of Aniono(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)zinc(II) Perchlorate Complexes in Nitromethane Solutions, and the Crystal and Molecular Structure of the Chloro-complex

By **Nathaniel W. Alcock, Norman Herron,** and **Peter Moore,*** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Variable-temperature ^{13}C n.m.r. spectroscopy in nitromethane solutions of the complex cations $[ZnX(L)]^+$ (X = Cl, Br, I, NCS, or ClO_4; L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) demonstrates the presence of a dynamic process which is not clearly seen in their corresponding 90-MHz ^{1}H n.m.r. spectra. Line-shape analysis shows that for X = Cl or NCS the activation parameters are $\Delta H^\ddagger = 59.3 \pm 3.2$ kJ mol^{-1} and $\Delta S^\ddagger = 15 \pm 12$ J K^{-1} mol^{-1} and $\Delta H^\ddagger = 49.5 \pm 1.8$ kJ mol^{-1} and $\Delta S^\ddagger = -10 \pm 10$ J K^{-1} mol^{-1} respectively. The dynamic process is interpreted as an intramolecular rearrangement between two identical trigonal-bipyramidal structures. The crystal structure of the complex $[ZnCl(L)][ClO_4]$ is, however, different to that proposed in solution. The complex crystallises in the monoclinic space group $P2_1$, $Z = 2$, with $a = 8.230(2)$, $b = 15.156(3)$, $c = 8.569(2)$ Å, and $\beta = 108.64(2)°$. 1 923 Reflections were recorded by four-circle diffractometer and least-squares refinement produced a final R of 0.041. In the crystal the complex has square-pyramidal geometry around the zinc atom with the four nitrogen atoms of the macrocycle forming the basal plane and the zinc centrally positioned 0.57 Å above the plane [Zn–N 2.20(1) Å]. The co-ordination sphere is completed by an apical chlorine atom [Zn–Cl 2.265(4) Å]. Possible reasons for the differing solution and crystal structures are discussed.

FIVE-CO-ORDINATE complexes of Ni^{II}, Zn^{II}, and Cu^{II} with the ligand 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane ($NN'N''N'''$-Me$_4$-cyclam, L) were first prepared in 1973.[1] The complexes were shown to be five-co-ordinate by a study of their magnetic properties, u.v.-visible spectra (Cu^{II} and Ni^{II}), and conductivity data in nitromethane solution, and their structures were deduced on the basis of the ^{1}H n.m.r. spectrum of $[ZnCl(L)][ClO_4]$ in [$^2H_3$]nitromethane which indicated that all the four N-methyl groups of L were magnetically equivalent. This allowed the assignment of a structure in which all the four methyl groups were on the same side of a plane defined by the four nitrogen atoms [the *trans*-I geometry of Bosnich *et al.*,[2] (1a)] and effectively excluded the possibility of any non-planar arrangement of the four nitrogen atoms, since this would necessarily cause inequivalence of the N-methyl groups and hence splitting of this resonance in the ^{1}H n.m.r. spectrum. The structure was therefore assigned as square pyramidal for the zinc(II) complex and the same structure was assumed for the nickel(II) and copper(II) complexes.

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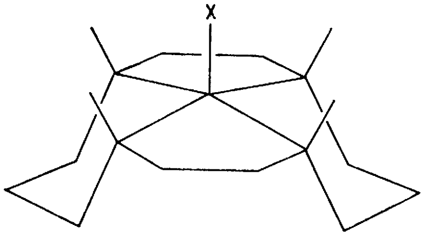
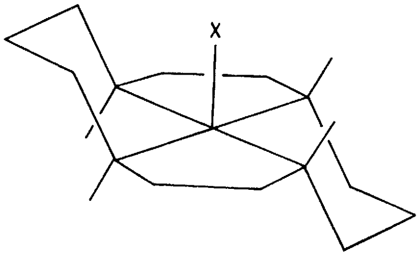
[1] E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.

[2] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.

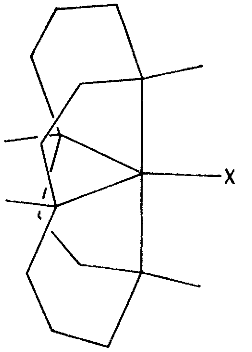
Later, however, a trigonal-bipyramidal geometry was postulated[3] for the nickel(II) complexes, based on the u.v.–visible spectra of these and related species, and a known trigonal-bipyramidal *X*-ray structure of a similar macrocyclic copper(II) complex.[4] Therefore, in an attempt to assign unambiguously the stereochemistry of these complexes, an *X*-ray structure analysis of [Ni(N_3)L][ClO$_4$] was completed which showed perfect square-pyramidal geometry.[5]



(1a)



(1b)



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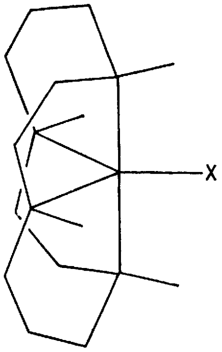

(1d)

Although this appeared to define the structure of these complexes completely, the ^{13}C n.m.r. spectra we have obtained for [ZnX(L)]$^+$ (X = Cl, Br, I, NCS, or ClO$_4$) in nitromethane solution indicate that a square-pyramidal geometry is less likely under these conditions, and reveal a dynamic process which previous ^1H n.m.r. studies failed to show. We report the results of our ^1H and ^{13}C n.m.r. studies, together with a comparison of the *X*-ray structure of [ZnCl(L)][ClO$_4$] with its structure in nitromethane solution as indicated by ^{13}C n.m.r. spectroscopy. This work forms part of our research into the co-ordination chemistry of heavier metal ions with macrocyclic ligands.[6]

EXPERIMENTAL

The complexes [ZnL][ClO$_4$]$_2$ and [ZnCl(L)][ClO$_4$] were prepared as previously described.[1] The complex [ZnI(L)][ClO$_4$] was precipitated by addition of an aqueous solution containing excess of AnalaR NaI to a saturated aqueous solution of [ZnL][ClO$_4$]$_2$. It was recrystallised from water, washed with ethanol and diethyl ether, and dried in air (Found: C, 30.4; H, 5.75; N, 10.25%. $C_{14}H_{32}ClIN_4O_4Zn$ requires C, 30.7; H, 5.85; N, 10.25%). Complexes [ZnX(L)][ClO$_4$] (X = Br or NCS) were prepared similarly using AnalaR NaBr or Na[NCS] respectively. Their purity was checked by ^1H and ^{13}C n.m.r. spectroscopy. The i.r. spectrum of [Zn(NCS)L][ClO$_4$] was recorded on a Perkin-Elmer 457 spectrophotometer; it includes a C–S stretching frequency at 804 cm^{-1}.

Carbon-13 (22.628-MHz) and ^1H (90-MHz) n.m.r. spectra were recorded in the range 223—323 K with a Bruker WH90 Fourier-transform spectrometer, using [$^2H_3$]nitromethane as a solvent and lock signal, and with a trace amount of dioxan as an internal shift marker. Temperatures at which the spectra were recorded were measured to ±0.5 °C using a calibrated Comark copper–constantan thermocouple.

Crystals of the complex [ZnCl(L)][ClO$_4$] suitable for *X*-ray diffraction were prepared by slow evaporation of an acetone solution to give clear hexagonal prisms.

Crystal Data.—$C_{14}H_{32}Cl_2N_4O_4Zn$, M = 456.4, Monoclinic, a = 8.230(2), b = 15.156(3), c = 8.569(2) Å, β = 108.64(2)°, U = 1 012.9(4) Å^3, θ_c = 18(2) °C, D_m = 1.50(5) g cm^{-3}, Z = 2, D_c = 1.496 g cm^{-3}, $F(000)$ = 480, space group $P2_1/m$ or $P2_1$, the latter confirmed by structural analysis, μ(Mo-K_α) = 15.32 cm^{-1}.

Data Collection.—A crystal of dimensions *ca.* 0·13 × 0.35 × 0.75 mm bounded by {010}{110}{011}{323} [see Table 1(*a*)] was examined on a Syntex $P2_1$ four-circle diffractometer. The unit-cell dimensions and their estimated standard deviations were obtained by a least-squares fit to 15 strong reflections with Mo-K_α graphite-monochromatised radiation (λ 0.709 26 Å). Systematic absence

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[3] R. Buxtorf, W. Steinmann, and T. A. Kaden, *Chimia*, 1974, **28**, 15.

[4] R. Bauer, W. Robinson, and D. Margerum, *J.C.S. Chem. Comm.*, 1973, 289.

[5] M. J. D'Aniello, M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Amer. Chem. Soc.*, 1975, **97**, 192.

[6] N. W. Alcock, N. Herron, and P. Moore, *J.C.S. Dalton*, 1978, 394.

$0k0$ for $k = 2n + 1$ indicated the space group $P2_1$ or $P2_1/m$, and crystal morphology indicated that the acentric group was more likely. Intensity data in the range $3 \leqslant 2\theta \leqslant 55°$ were recorded by the θ—2θ scan technique and three check reflections were monitored every 100 measurements. A decay of *ca.* 10% in the intensities of these standards during data collection was corrected during data processing. 1 923 Reflections with $I/\sigma(I) \geqslant 3.0$ were recorded and corrected for absorption by the method of Alcock [7] to give transmission factors in the range 0.59—0.82.

Structure Solution and Refinement.—The structure was solved by the heavy-atom method using a three-dimensional Patterson synthesis to locate the position of the zinc atom. The remaining non-hydrogen atoms were located in subsequent electron-density maps and all the atoms were refined by minimising the function $\Sigma(|F_o| - |F_c|)^2$. Refinement was carried out in the acentric space group $P2_1$ and this was satisfactory once the pseudo-mirror symmetry imposed by the zinc atom had been broken. Refinement by the least-squares method with all the non-hydrogen atoms anisotropic gave an R value $[= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ of 0.041. Weighting analysis indicated that unit weights were satisfactory.

TABLE 1

X-Ray analysis of $[ZnCl(L)][ClO_4]$

(*a*) Miller indices and origin–plane distances for the facial planes of the crystal

h	*k*	*l*	*d*/cm	*h*	*k*	*l*	*d*/cm
0	1	0	0.007 8	0	1	−1	0.032 6
0	−1	0	0.005 9	0	−1	−1	0.032 5
1	−1	0	0.017 4	0	1	1	0.009 7
−1	1	0	0.017 0	−3	2	3	0.012 6
0	−1	1	0.008 3	3	2	−3	0.033 9

(*b*) Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Zn	1 300(1)	2 500	3 681(1)
Cl(1)	−132(4)	1 685(2)	5 033(4)
Cl(2)	4 222(4)	4 753(2)	707(4)
N(1)	3 973(11)	2 352(7)	5 276(12)
N(2)	2 175(12)	1 576(7)	2 118(12)
N(3)	9 283(13)	2 991(7)	1 507(12)
N(4)	1 227(14)	3 836(6)	4 619(14)
O(1)	5 425(16)	4 815(9)	2 344(14)
O(2)	7 219(16)	252(11)	9 382(22)
O(3)	5 018(26)	−41(15)	407(18)
O(4)	3 694(19)	3 864(8)	486(19)
C(1)	4 649(19)	1 528(10)	4 658(19)
C(2)	4 134(17)	1 559(10)	2 873(17)
C(3)	1 805(16)	1 823(9)	331(15)
C(4)	−9(18)	2 047(10)	9 452(17)
C(5)	9 498(18)	2 965(10)	−71(18)
C(6)	9 279(20)	4 014(11)	1 834(20)
C(7)	9 597(24)	4 200(13)	3 455(24)
C(8)	2 752(17)	4 368(9)	4 704(16)
C(9)	4 475(16)	3 985(9)	5 880(15)
C(10)	5 051(16)	3 148(8)	5 213(16)
C(11)	4 166(18)	2 134(9)	7 040(17)
C(22)	1 473(17)	693(10)	2 186(15)
C(33)	−2 344(14)	2 685(7)	1 427(13)
C(44)	1 005(18)	3 838(10)	6 285(17)

Scattering factors and anomalous dispersion factors from ref. 8 were used, and all computation was carried out with the '*X*-RAY '76' programs [9] on a Burroughs B6700 computer. Final co-ordinates are in Table 1(*b*). Structure factors and temperature factors are listed in Supplementary Publication No. SUP 22294 (19 pp.).* Bond lengths and angles are in Table 2(*a*) and (*b*) respectively.

TABLE 2

(*a*) Bond lengths (Å) and angles (°) with standard deviations in parentheses

Zn–Cl(1)	2.265(4)	N(3)–C(6)	1.57(2)
Zn–N(1)	2.199(8)	N(3)–C(33)	1.40(2)
Zn–N(2)	2.211(11)	N(4)–C(7)	1.50(2)
Zn–N(3)	2.192(9)	N(4)–C(8)	1.47(2)
Zn–N(4)	2.186(10)	N(4)–C(44)	1.50(2)
N(1)–C(1)	1.53(2)	C(1)–C(2)	1.45(2)
N(1)–C(10)	1.51(2)	C(3)–C(4)	1.48(2)
N(1)–C(11)	1.50(2)	C(4)–C(5)	1.54(2)
N(2)–C(2)	1.53(2)	C(6)–C(7)	1.36(2)
N(2)–C(3)	1.51(2)	C(8)–C(9)	1.57(3)
N(2)–C(22)	1.47(2)	C(9)–C(10)	1.53(2)
N(3)–C(5)	1.42(2)		

(*b*) Bond angles

Cl(1)–Zn–N(1)	102.0(3)	Zn–N(1)–C(11)	114.2(8)
Cl(1)–Zn–N(2)	106.7(3)	C(1)–N(1)–C(10)	111(1)
Cl(1)–Zn–N(3)	104.1(3)	C(1)–N(1)–C(11)	104(1)
Cl(1)–Zn–N(4)	103.7(4)	C(10)–N(1)–C(11)	110(1)
N(1)–Zn–N(2)	81.8(4)	Zn–N(2)–C(2)	104.9(7)
N(1)–Zn–N(3)	153.9(4)	Zn–N(2)–C(3)	117.3(7)
N(1)–Zn–N(4)	90.3(4)	Zn–N(2)–C(22)	110.2(9)
N(2)–Zn–N(3)	90.3(4)	C(2)–N(2)–C(3)	106(1)
N(2)–Zn–N(4)	150.0(4)	C(2)–N(2)–C(22)	110(1)
N(3)–Zn–N(4)	84.0(4)	C(3)–N(2)–C(22)	108.2(9)
Zn–N(1)–C(1)	105.7(7)	Zn–N(3)–C(5)	120.6(8)
Zn–N(1)–C(10)	112.3(7)	Zn–N(3)–C(6)	103.1(7)
Zn–N(3)–C(33)	112.5(8)	N(1)–C(1)–C(2)	109(1)
C(5)–N(3)–C(6)	102(1)	N(2)–C(2)–C(1)	111(1)
C(5)–N(3)–C(33)	110.7(9)	N(2)–C(3)–C(4)	115(1)
C(6)–N(3)–C(33)	106(1)	C(3)–C(4)–C(5)	112(1)
Zn–N(4)–C(7)	102.7(9)	N(3)–C(5)–C(4)	114(1)
Zn–N(4)–C(8)	113.7(9)	N(3)–C(6)–C(7)	112(1)
Zn–N(4)–C(44)	112.3(8)	N(4)–C(7)–C(6)	116(2)
C(7)–N(4)–C(8)	113(1)	N(4)–C(8)–C(9)	114(1)
C(7)–N(4)–C(44)	106(1)	C(8)–C(9)–C(10)	113(1)
C(8)–N(4)–C(44)	108(1)	N(1)–C(10)–C(9)	113(1)

RESULTS AND DISCUSSION

Solution Structure.—Conductivity studies [1] have shown that $[MX(L)][ClO_4]$ (M = Ni, Cu, or Zn; X = Cl, Br, or NCS) are 1 : 1 electrolytes in nitromethane solution and, therefore, the co-ordinated anion X is not ionised on dissolution in this solvent. A variable-temperature ^1H n.m.r. study in the range 323 —223 K (the freezing point of the solutions in $[^2H_3]$nitromethane) of the complexes $[ZnX(L)][ClO_4]$ (X = Cl, Br, or I) shows no splitting or broadening of the macrocycle *N*-methyl resonance, which remains a sharp singlet. This behaviour is identical to that observed previously [1] for the chloro-complex, apparently indicating the absence of any dynamic process involving folding of the macrocycle from a conformation with a rigid planar array of co-ordinated nitrogen atoms; this therefore implies square-pyramidal co-ordination of the zinc atom (1a). The complex with X = NCS, however, does show slight broadening and eventually an ill resolved splitting of the *N*-methyl ^1H resonance at 223 K with a separation of <3 Hz (at 90 MHz).

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[7] N. W. Alcock, in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

[8] 'International Tables for *X*-ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[9] TR-446, March 1976.

A ^{13}C n.m.r. study of the same solutions reveals the presence of a dynamic process much more clearly, as shown in Figure 1. At 323 K the ^{13}C spectra of all the complexes consist of the expected four sharp lines, with an assignment based on integrals and proton-coupled spectra as shown in Figure 1. On cooling to 303 K, however, each of the resonances due to carbon atoms *b*—*d* begin to broaden, and on further cooling eventually split into two sharp lines of equal population (Figure 1).

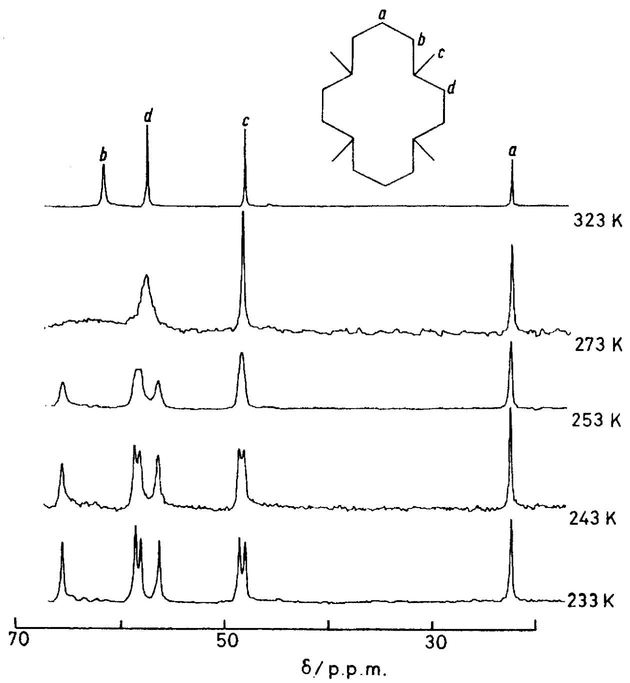

FIGURE 1 Variable-temperature ^{1}H-decoupled ^{13}C n.m.r. spectra of $[ZnI(L)][ClO_4]$ in $[^{2}H_3]$nitromethane solution, with assignment of resonances (chemical shifts relative to internal dioxan at δ 67.3 p.p.m.)

This behaviour is observed for all the complexes studied (X = Cl, Br, I, NCS, or ClO_4) and in Table 3 are listed the magnitudes of the splittings of the three high-temperature resonances *b*—*d* at the limit of slow exchange (233 K).

TABLE 3

Carbon-13 chemical shifts (δ/p.p.m. relative to internal dioxan at δ 67.3 p.p.m.) at 233 K for the cations $[ZnX(L)]^+$ (for assignments see Figure 1)

Anion X	*a*	*b*	*c*	*d*
ClO_4	21.4	63.7, 58.8	46.3, 42.5	57.3, 56.5
Cl	21.6	64.2, 57.7	46.5, 44.0	57.7, 55.7
Br	21.6	64.5, 57.7	47.0, 45.2	57.5, 55.6
I	21.5	64.7, 57.2	47.8, 47.2	57.7, 55.4
NCS	21.6	64.3, 58.0	46.2, 42.9	57.7, 55.9

The observed dynamic process is best understood by considering the behaviour of the *N*-methyl resonance *c* over the temperature range studied. At 233 K this resonance splits into two peaks of equal intensity which indicates that the four methyl groups form two magnetically distinct pairs. The integral of each of these two peaks is the same as that of resonance *a*, which is known to arise from two carbon atoms. This, together with the absence of a splitting for resonance *a*, strongly implies that the dynamic behaviour of L arises from an intra- and not an inter-molecular process. There are three possible intramolecular structural processes which would cause equal splitting of the *N*-methyl resonances at the limit of slow exchange.

(*i*) If the complex were square pyramidal in solution with structure (1b) then the *N*-methyl groups would form two distinct pairs in the slow-exchange limit, and on accelerating the rate of exchange of ligand X, these pairs would become equivalent. This explanation is, however, readily dismissed because such a slow-exchange process is unlikely for Zn^{II}, and the structure observed in the limit of slow exchange would undoubtedly cause splitting of resonance *a* into two peaks of equal area *as well as* all the other resonances *b*—*d*. Also, one can see no reason why such a structure should be five-co-ordinate, since ligand X must necessarily co-ordinate with equal ease on both sides of the L plane. Finally, structure (1b) has not been observed for complexes of L prepared in this way, crystal structures of $[Ni(N_3)L]^+$ (ref. 5) and $[ZnCl(L)]^+$ complexes showing structure (1a); there are no low-energy processes by which (1a) and (1b) can be interconverted.

(*ii*) Other explanations of the observed splitting are possible if the macrocycle L is non-planar. Two such structures are shown in (1c) and (1d); both have the complex effectively trigonal bipyramidal with X equatorial. We can see that structure (1c) will give two pairs of non-equivalent *N*-methyl groups as required. However, to interconvert these pairs, and hence make them equivalent, we must envisage a process such as that schematically illustrated in (*a*) in the Scheme. This macrocycle geometry can be viewed as a distorted version of a *cis*-octahedral structure, the set of nitrogen configurations being the same as that observed for a *cis* complex of the analogous macrocycle 1,4,8,11-tetra-azacyclotetradecane (cyclam) in $[Co(cyclam)(en)]Cl_3$ (en = ethylenediamine).[10] However, no *cis*-type complexes of L have yet been prepared, probably because it has been shown that complexes prepared by direct combination of a metal ion with L have a kinetically determined set of nitrogen configurations inconsistent with a *cis*-macrocycle geometry.[1] Also, since the crystals obtained from these solutions contain L with the *trans*-I set of nitrogen configurations [2] (see below), it is difficult to see why simple solution in a non-co-ordinating solvent should promote such drastic and complete conversion into a structure where alternate methyl groups are above and below the macrocycle plane. Such a conversion would require at least two nitrogen configurational inversions for which there is no available route other than bond cleavage.

(*iii*) A much more likely trigonal-bipyramidal geometry is illustrated in (1d); whereas structure (1c) could be regarded as a distorted *cis* complex, (1d) is best thought of as a distorted square pyramid. It is clear

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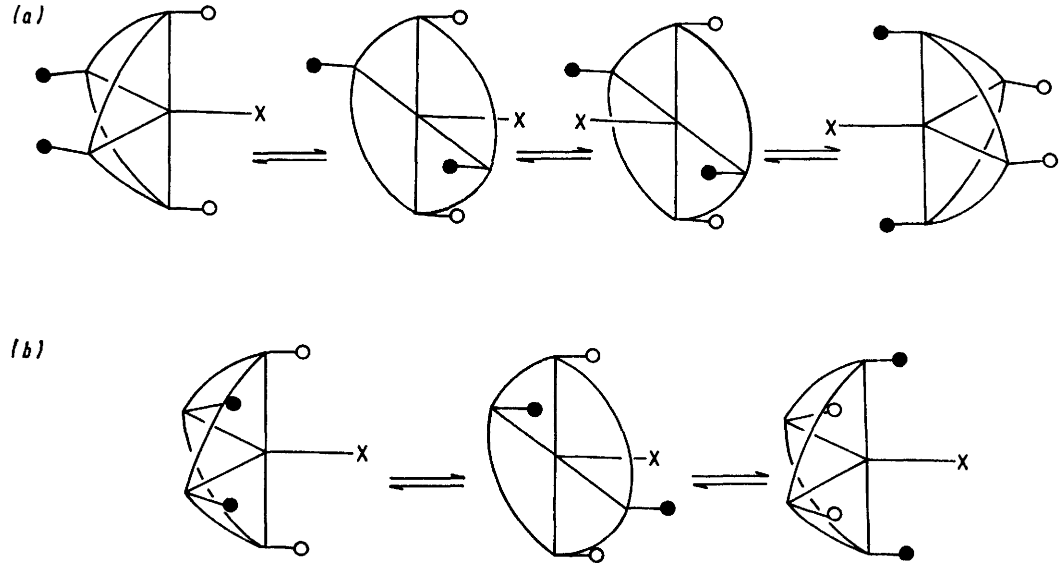
[10] T. F. Lai and C. K. Poon, *Inorg. Chem.*, 1976, **15**, 1562.

that (1d) has a macrocycle conformation consistent with the slow-exchange ^{13}C n.m.r. spectrum, the two axial *N*-methyl groups being magnetically distinct from the two equatorial groups, causing the required splitting pattern. The exchange process required to interconvert these axial and equatorial *N*-methyls and so make them equivalent in the fast-exchange n.m.r. limit is illustrated in (*b*) in the Scheme. We can immediately see the plausibility of this type of scheme to explain the observed ready dynamic process in that (*a*) no bond cleavage is necessary, (*b*) relatively small bond rotations about the central metal are required, and (*c*) the proposed transition state is identical to the observed crystal structures of this type of complex (see below).

A referee has pointed out that there is a fourth possible interpretation of the ^{13}C n.m.r. data. This explanation assumes that the complex has a square-pyramidal structure identical to that found in the crystal structure (Figure 2). It is clear in Figure 2 that the conformation of the five-membered chelate rings is such that carbon atoms C(1) and C(7) form a magnetically equivalent pair, distinct from the pair C(2) and C(6). This conformational difference within the five-membered rings may therefore explain the observed low-temperature splitting of the ^{13}C resonance *d* (Figure 1) attributed to them, and therefore lead to the associated splitting of the other ^{13}C resonances *b* and *c*. On increasing the temperature it is reasonable to expect that conformational ' flipping ' in the five-membered chelate rings will be accelerated to the point where it becomes sufficiently rapid to average the magnetic environments of all the four carbon atoms C(1), C(2), C(6), and C(7). This will cause the collapse of the doublet resonance *d* to a singlet and also remove the associated splittings of resonances *b* and *c* (Figure 1) in the high-temperature limit. This interpretation is therefore consistent with the reported data and has the additional attraction, over the alternative explanation (*iii*) above, that it requires no modification of the solid-state structure on solution in nitromethane.



Scheme

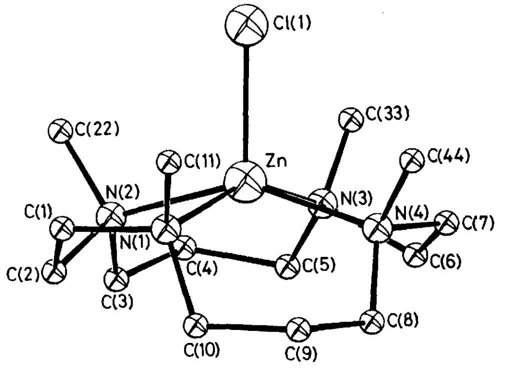


Figure 2 Molecular structure of the $[ZnCl(L)]^+$ cation

We feel, however, that this explanation, although plausible, has several inconsistencies which indicate it to be less likely than explanation (*iii*) above. Perhaps the greatest of these concerns other work we have carried out with diamagnetic square-planar $[NiL][ClO_4]_2$. In this complex the perchlorate ions are unco-ordinated and the macrocyclic ligand has the same configuration as that found here for the zinc complex.[1,5] This four-co-ordinate nickel(II) complex shows no dynamic behaviour whatsoever in its ^{13}C n.m.r. spectra down to 230 K. However, when the analogous chloro-complex $[NiCl(L)][ClO_4]$ is examined the dynamic behaviour is restored and is qualitatively similar to that found for the zinc complexes. This strongly indicates that the dynamic process depends directly on the presence of a fifth ligand in the metal co-ordination sphere, and is not simply a function of the macrocyclic framework conformations which we therefore predict to be interconverting in solution too rapidly to be detectable in the temperature range employed here. The magnitude of the splittings observed in the ' frozen-out ' spectra of $[Zn(L)X]^+$ ions (Table 3) are also greater than we would expect for a square-pyramidal structure, and more consistent with the folded macrocycle configuration in structure (1d).

We therefore propose that the solution structures of complexes of the type $[ZnX(L)][ClO_4]$ are rapidly interconverting trigonal bipyramids. The activation parameters of this dynamic process were obtained by a full line-shape analysis, following the method of Moore,[11] of the ^{13}C n.m.r. resonances *b*—*d* (Figure 1) for the complexes where X = Cl or NCS over the range 233—293 K. The results show that $\Delta H^{\ddagger} = 59.3 \pm 3.2$ and 49.5 ± 1.5 kJ mol^{-1} and $\Delta S^{\ddagger} = 15 \pm 12$ and -10 ± 10 J K^{-1} mol^{-1} for X = Cl and NCS respectively. We can see that the two complexes have comparable activation parameters. The small differences may be explained in terms of the greater size of the chlorine atom compared to the thiocyanate N atom (the i.r. spectrum shows the C–S stretching frequency to be at 804 cm^{-1}, indicative of *N*-bound thiocyanate [12] as compared to *S*-bound thiocyanate which has a C–S stretch at *ca.* 700 cm^{-1}) which will therefore tend to disfavour the exchange transition state [Scheme (*b*)] because of greater steric interactions of the chlorine with the *N*-methyl groups.

Crystal Structure.—In order to investigate the $[ZnX(L)][ClO_4]$ system fully a crystal structure of the complex (X = Cl) was undertaken for comparison with the proposed solution structure. The complex has an almost perfect square-pyramidal geometry (Figure 2) with the four nitrogen atoms, N(1)—N(4), of the ligand L forming the basal plane (±0.1 Å) above which the zinc atom is centrally displaced by 0.57 Å. A chlorine atom, Cl(1), is apically co-ordinated to complete the structure at a normal [13] Zn–Cl distance [2.265(4) Å]. In this structure we see that the ligand L has the *trans*-I structure [2] (1a) previously observed in the azidonickel complex.[5] A comparison of these two structures indicates further close similarities. In both, the metal atom is found to move out of the macrocyclic plane towards the apical ligand, by 0.57 Å for the zinc complex compared to 0.33 Å for the nickel complex. This increase with zinc is consistent with its larger ionic radius and is reflected in the metal–nitrogen distances [Zn–N 2.20(1), Ni–N 2.10(1) Å]. Most of the bond angles and distances within the ligands L of both complexes have normal values although small deviations, probably due to strain, are present in the five-membered chelate rings; for example, C(1)–C(2) (1.45 Å) and C(6)–C(7) (1.36 Å) are both slightly shorter than expected, as are the corresponding distances in the nickel structure. The dihedral angles (Table 4) are also indicative of this strain in the five-membered chelate rings, especially that containing C(6) and C(7). The crystal-packing diagram (Figure 3) shows that the isolated cations are flanked by unco-ordinated perchlorate anions; the crystal forces between the ions must be mainly electrostatic. This solid-phase structure is therefore inconsistent with that proposed in solution.

Comparison and Rationalisation of Structures.—The solution- and solid-phase structures [(1d) and (1a) respectively] of these complexes can be seen to be two modifications of the same basic macrocyclic conformation. In both structures the nitrogen atoms have the same configuration (all the four methyl groups on the same side of the macrocycle) so that one could reasonably expect interconversion between them to be a relatively low-energy process.

TABLE 4

Dihedral angles (°) with standard deviations in parentheses

C(1)–C(2)–N(2)–C(3)	167(1)	C(9)–C(10)–N(1)–C(1)	178(1)
C(2)–N(2)–C(3)–C(4)	140(2)	C(10)–N(1)–C(1)–C(2)	77(1)
N(2)–C(3)–C(4)–C(5)	58(1)	N(1)–C(1)–C(2)–N(2)	61(1)
C(3)–C(4)–C(5)–N(3)	177(2)	C(11)–N(1)–C(10)–C(9)	64(1)
C(4)–C(5)–N(3)–C(6)	107(1)	C(11)–N(1)–C(1)–C(2)	166(1)
C(5)–N(3)–C(6)–C(7)	162(1)	C(22)–N(2)–C(2)–C(1)	76(1)
N(3)–C(6)–C(7)–N(4)	85(1)	C(22)–N(2)–C(3)–C(4)	102(1)
C(6)–C(7)–N(4)–C(8)	121(2)	C(33)–N(3)–C(5)–C(4)	12(1)
C(7)–N(4)–C(8)–C(9)	60(1)	C(33)–N(3)–C(6)–C(7)	83(1)
N(4)–C(8)–C(9)–C(10)	71(2)	C(44)–N(4)–C(7)–C(7)	169(1)
C(8)–C(9)–C(10)–N(1)	72(1)	C(44)–N(4)–C(8)–C(9)	64(1)

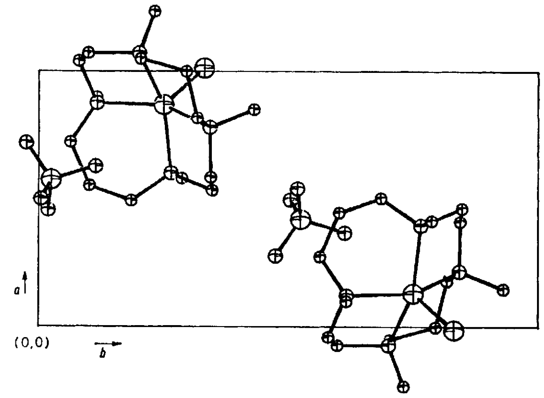


FIGURE 3 Crystal-packing diagram for $[ZnCl(L)][ClO_4]$ viewed along the *c* axis

Looking first at the solution structure (1d) we can see that co-ordination of the anion X has forced the macrocycle to fold, pushing back two of its nitrogen atoms to form a trigonal-bipyramidal complex. The structure has the advantage that it lessens any steric conflict between the anion X and the four *N*-methyl groups as these two are moved out of the plane. Molecular models confirm that this arrangement does indeed reduce steric contact over that of a square-pyramidal geometry. We can therefore readily understand the folded solution structure and also the slight dependence on X of the $\Delta H^{\ddagger}$ values for the exchange process.

In the crystal structure we had expected to find the same structure as that in solution. However, as is often

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[11] P. Moore, *J.C.S. Faraday*, 1976, 826.

[12] K. Nakamoto, ' Infra-Red Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970, p. 187.

[13] ' Interatomic Distances Supplement,' ed. L. E. Sutton, *Special Publ.*, The Chemical Society, London, 1965, no. 18, p. S13s.

the case, simple steric arguments must be tempered with a consideration of the effects of crystal-packing forces, where the relatively close approach of other anions and cations may easily modify a structure. Also, the absence of any solvent in the crystal means that we are comparing an unsolvated ion with the solvated solution form. The barrier to interconversion between structures (1d) and (1a) is low, as indicated by $\Delta H^{\ddagger}$, and the small energy difference between the structures has been interchanged such that the square-pyramidal form is now the most stable in the solid state. We observe, therefore, that the crystal structure is, in fact, an almost perfect transition state for the observed solution dynamics [Scheme (*b*)]. The *trans* N–Zn–N angles of 154 and 149° of the square-pyramidal crystal structure are exactly intermediate between the required ideal trigonal-bipyramidal angles of 180 and 120°.

We therefore conclude that the solution and crystallographic structures of the $[ZnX(L)][ClO_4]$ system are trigonal bipyramidal (1d) and square-pyramidal (1a) respectively, but that conversion between them is a relatively low-energy process as confirmed by the estimate of $\Delta H^{\ddagger}$ for the interconversion in solution. In a sense this vindicates the apparently diverse findings of previous workers,[1,3,5] The present results show the importance of obtaining, if possible, both the ^{1}H and ^{13}C n.m.r. spectra in studies of this type. The greater chemical-shift scale available in ^{13}C n.m.r. studies may, as in this case, reveal structural information which is easily missed in any ^{1}H n.m.r. spectrum.

Preliminary results for the L complexes of Cd^{II}, Hg^{II}, and Ni^{II} indicate the presence of identical behaviour in solution to that observed here, and with comparable energy profiles, and this will be reported later, together with further studies of macrocyclic complexes involving the ligand 1,4,8,11-tetra-azacyclotetradecane co-ordinated to Zn^{II}, Cd^{II}, Hg^{II}, Ni^{II}, and Pb^{II}.

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