Structural and Dynamic Behaviour of Complexes of Lead(II) with Two Tetra-aza Macrocyclic Ligands as studied by *X*-Ray Crystallography and Natural-abundance Carbon-13 and Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy

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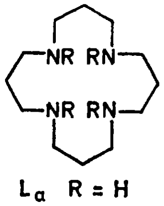
Two complexes of the type $[PbL][NO_3]_2$, where L = L_a = 1,4,8,11-tetra-azacyclotetradecane or L_b = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, have been investigated by n.m.r. techniques in dimethyl sulphoxide (dmso) solution. The complex where L = L_a is interpreted as adopting a *cis*-octahedral geometry with a folded macrocyclic ligand. This geometry is confirmed by an *X*-ray analysis which also identifies unsymmetrical bidentate nitrate ions in *cis* positions. The asymmetry of these groups is probably caused by the lone pair on Pb^{II}. The complex crystallises in the monoclinic space group $P2_1/c$, $Z = 4$, with $a = 10.326(2)$, $b = 11.145(3)$, $c = 14.832(4)$ Å, and $\beta = 96.19(2)°$. 1 909 Reflections with $I/\sigma(I) > 3.0$ have been recorded on a four-circle diffractometer and least-squares refinement produced a final R of 0.049. The n.m.r. data reveal high-temperature, dynamic, conformational changes, and two strikingly different $^1J(^{207}Pb-^{15}N)$ coupling constants (207.5 and 19.8 Hz) at low temperatures. The dynamic process, with $\Delta H^\ddagger = 110 \pm 10$ kJ mol^{-1} and $\Delta S^\ddagger = 105 \pm 20$ J K^{-1} mol^{-1}, is interpreted as an intramolecular rearrangement between two identical cisoid structures, while the differing coupling constants for axial and equatorial nitrogen atoms are believed to be a consequence of the axial distortion observed in the crystal structure. When L = L_b the complex is not very stable in dmso ($K = 1.31$ dm^3 mol^{-1} at 298 K) and macrocycle exchange is found to occur at ambient temperatures ($\Delta H^\ddagger = 38.5 \pm 0.7$ kJ mol^{-1}, $\Delta S^\ddagger = -70 \pm 3$ J K^{-1} mol^{-1}). The structure and behaviour of both complexes are discussed in relation to the ionic radius of the lead(II) ion.

ALTHOUGH transition-metal complexes of the macrocyclic ligands L_a and L_b have been extensively investigated in recent years, no complexes with non-transition metals have been reported. We have, therefore, attempted to synthesise such complexes with lead(II) as part of our studies on the co-ordination chemistry of heavy-metal ion–macrocycle complexes.[1] For complexes of the macrocycle L_a, five possible strain-free octahedral geometries have been predicted, four of which involve *trans* square-planar co-ordination (differing in their relative configurations at the co-ordinated nitrogen atoms) and the fifth a *cis* conformation of the ligand. Only one *trans* geometry has been observed in practice *trans*-III,[2,3] whilst the folded *cis* geometry has only been found with inert metal ions such as cobalt(III),[4] rhodium(III),[5] and chromium(III).[6] For the lead(II) ion, the ionic radius (1.21 Å) is too large to be accommodated within the ring of a 14-membered macrocycle in a regular square-planar geometry,[7] and so some deviation of the complex, away from a planar array of lead and nitrogen atoms, may be expected.



L_a R = H
L_b R = Me

Complexes of L_b, the *N*-tetramethylated analogue of L_a, almost invariably adopt a five-co-ordinate geometry,[8,9] the sixth octahedral co-ordination site being sterically blocked by the alkyl backbone of the macrocycle. Such a geometry is presumed to be kinetically determined.[10]

Synthesis and structural elucidation of the complexes of lead(II) with the closely related macrocycles L_a and L_b would therefore be expected to provide a useful comparison of how co-ordinative preferences are modified to accommodate large metal ions, providing further pointers to the factors which dictate the mode of macrocycle co-ordination.[1] A multinuclear n.m.r. and *X*-ray crystallographic approach to the problem has been applied and the results of these investigations are now reported.

EXPERIMENTAL

The complex $[Pb(L_a)][NO_3]_2$ was prepared by dissolving 0.622 g of powdered AnalaR lead(II) nitrate in dry dimethyl sulphoxide (dmso) (5 cm^3) and adding solid L_a (0.4 g).[11] The resulting slurry was stirred for 1 h at room temperature, after which time the clear solution could be reduced to a volume of *ca.* 2 cm^3 under vacuum and the complex precipitated with dry AnalaR methanol. The resulting fine white powder was recrystallised from dmso–methanol (1 : 1), washed with diethyl ether, and dried over P_2O_5 in a vacuum desiccator, yield 0.94 g (88.5%) {Found: C, 21.2; H, 4.50; N, 15.8; Pb, 39.0. Calc. for $[Pb(L_a)][NO_3]_2$: C, 21.8; H, 4.35; N, 15.5; Pb, 39.3%}. The complex may only be prepared using dried reagents and is appreciably soluble only in dmso (>1 mol dm^{-3}). The molar conductivity of a 0.002 mol dm^{-3} solution in dmso at 18.4 ± 0.2 °C is 7.3(3) × 10^{-2} S m^2 mol^{-1}, consistent with a 2 : 1 electrolyte. The i.r. spectrum of the solid complex shows ν(NH) at 3 220 and ν(NO_3) at 1 360, 1 299, 998, 795, and 720 cm^{-1} consistent with unidentate or unsymmetrical bidentate nitrate co-ordination.[12]

The complex $[Pb(L_b)][NO_3]_2$ was prepared as described above for the L_a complex, using 0.51 g of L_b.[13] The dmso was completely removed by vacuum distillation at room temperature to leave a crystalline white complex {Found: Pb, 35.8. Calc. for $[Pb(L_b)][NO_3]_2$: Pb, 35.3%}. The complex very readily dissociates and will only dissolve in dry dmso. The molar conductivity of a 0.002 mol dm^{-3}

solution in dmso at 18.4 ± 0.2 °C is $7.3(3) \times 10^{-2}$ S m^2 mol^{-1}, again indicating a 2 : 1 electrolyte. The solid has a very complex i.r. spectrum associated with the nitrate moieties which may well be due to a mixture of unidentate and free nitrate ions.

Natural-abundance ^{13}C (22.63-MHz) and ^{15}N (18.24-MHz) n.m.r. spectra were recorded in the temperature range 253—433 K with a Bruker WH90 FT spectrometer (^{13}C), and at 300 K with a Bruker WH180 FT spectrometer (^{15}N). $[^2H_6]$Dimethyl sulphoxide was used as a solvent and lock signal, with *ca.* 5% dioxan (^{13}C) or external $[^{15}N]CD_3NO_2$ (^{15}N) as a shift reference. Temperatures were measured to ±0.5 °C using a calibrated Comark copper–constantan thermocouple, and were held constant with a standard Bruker temperature-control unit (±0.5 °C). Infrared spectra were recorded of Nujol mulls using a Perkin-Elmer 457 spectrometer and CsI windows, and conductivity measurements were performed with a Phillips PR 9500 conductivity bridge. Metal analyses were carried out with a Varian AA6 atomic absorption spectrophotometer.

Crystals of the complex $[Pb(L_a)][NO_3]_2$ suitable for *X*-ray diffraction were prepared by slow cooling of a saturated dmso–methanol (1 : 1) solution to give small clear laths.

Crystal Data.—$C_{10}H_{24}N_6O_6Pb$, $M = 531.2$, Monoclinic, $a = 10.326(2)$, $b = 11.145(3)$, $c = 14.832(4)$ Å, $\beta = 96.19(2)°$, $U = 1\,697.0(7)$ Å^3, $T = 18(2)$ °C, $D_m = 2.12(5)$ g cm^{-3}, $Z = 4$, $D_c = 2.08$ g cm^{-3}, $F(000) = 1\,024$, space group $P2_1/c$, $\mu(\text{Mo-}K_\alpha) = 100.61$ cm^{-1}.

Data Collection.—A crystal of dimensions *ca.* $0.06 \times 0.10 \times 0.25$ mm bounded by $\{011\}\{211\}\{120\}$ was examined with a Syntex $P2_1$ four-circle automated diffractometer. The unit-cell dimensions and their estimated standard deviations (e.s.d.s) were obtained by a least-squares fit to 15 strong reflections with Mo-K_α graphite-monochromatised radiation ($\lambda = 0.709\,26$ Å). Systematic absences, $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, indicate the space group $P2_1/c$. Intensity data in the range $3 \leqslant 2\theta \leqslant 55°$ were collected by the θ—2θ scan technique and three check reflections were monitored every 100 reflections. 1 909 Reflections with $I \geqslant 3.0\sigma(I)$ were recorded and corrected for absorption by the method of Alcock [14] to give transmission factors in the range 0.397—0.604.

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 lead atom. All remaining non-hydrogen atoms were located in subsequent electron-density maps and all atoms were refined by minimising the function $\Sigma(|F_o| - |F_c|)^2$. Refinement by the least-squares method with anisotropic temperature factors for all atoms gave R 0.049.

Scattering factors and anomalous dispersion factors [15] were used, and all computing was performed with a Burroughs B6700 computer, using the '*X*-RAY '76' programs.[16] Final atomic co-ordinates are in Table 1. Structure factors and temperature factors are listed in Supplementary Publication No. 22556 (15 pp.).† Bond lengths and angles are included in Table 2(*a*) and (*b*) respectively.

RESULTS AND DISCUSSION

$[Pb(L_a)][NO_3]_2$.—Previous attempts at the preparation of this complex by other workers failed to produce any

TABLE 1

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

Atom	*X*	*Y*	*Z*
Pb	2 263.0(6)	4 051.3(5)	669.4(4)
N(1)	2 013(14)	3 867(11)	2 275(9)
N(2)	4 452(16)	4 048(17)	1 532(13)
N(3)	2 822(14)	1 896(10)	809(9)
N(4)	163(15)	2 822(17)	741(12)
C(1)	3 114(42)	4 482(30)	2 759(24)
C(2)	4 378(33)	3 901(37)	2 506(24)
C(3)	5 432(41)	3 316(43)	1 150(38)
C(4)	5 233(35)	2 025(46)	1 014(28)
C(5)	4 048(22)	1 572(17)	453(13)
C(6)	1 655(25)	1 207(14)	415(15)
C(7)	475(32)	1 535(31)	902(23)
C(8)	9 187(34)	3 367(43)	1 273(30)
C(9)	9 601(33)	3 470(42)	2 258(29)
C(10)	704(35)	4 370(24)	2 529(19)
N(5)	7 639(19)	2 155(15)	4 013(12)
O(1)	8 649(27)	1 512(21)	3 998(17)
O(2)	6 590(32)	1 731(29)	3 703(24)
O(3)	7 690(35)	3 173(18)	4 293(21)
N(6)	2 938(15)	1 177(13)	3 510(10)
O(4)	3 707(21)	841(28)	4 117(14)
O(5)	2 016(24)	1 805(21)	3 687(17)
O(6)	3 080(30)	931(26)	2 708(12)

TABLE 2

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

(*a*) Lengths

Pb–N(1)	2.43(1)	N(4)–C(7)	1.48(4)
Pb–N(2)	2.47(2)	N(4)–C(8)	1.48(5)
Pb–N(3)	2.47(1)	N(5)–O(1)	1.27(3)
Pb–N(4)	2.58(2)	N(5)–O(2)	1.23(4)
Pb–O(1)	2.96(2)	N(5)–O(3)	1.21(3)
Pb–O(2)	3.31(3)	N(6)–O(4)	1.20(3)
Pb–O(4)	2.88(2)	N(6)–O(5)	1.23(3)
Pb–O(5)	3.08(2)	N(6)–O(6)	1.25(2)
N(1)–C(1)	1.45(4)	C(1)–C(2)	1.54(6)
N(1)–C(10)	1.55(4)	C(3)–C(4)	1.46(7)
N(2)–C(2)	1.46(4)	C(4)–C(5)	1.49(4)
N(2)–C(3)	1.46(5)	C(6)–C(7)	1.53(4)
N(3)–C(5)	1.47(3)	C(8)–C(9)	1.48(6)
N(3)–C(6)	1.49(3)	C(9)–C(10)	1.54(5)

(*b*) Angles

N(1)–Pb–N(2)	71.4(6)	C(2)–N(2)–Pb	112(2)
N(1)–Pb–N(3)	83.3(4)	C(3)–N(2)–Pb	116(2)
N(1)–Pb–N(4)	74.7(5)	C(2)–N(2)–C(3)	116(3)
N(1)–Pb–O(1)	81.2(6)	C(5)–N(3)–Pb	114(1)
N(1)–Pb–O(4)	154.9(5)	C(6)–N(3)–Pb	107(1)
N(2)–Pb–N(3)	76.3(5)	C(5)–N(3)–C(6)	115(1)
N(2)–Pb–N(4)	134.7(6)	C(7)–N(4)–Pb	111(1)
N(2)–Pb–O(1)	101.8(7)	C(8)–N(4)–Pb	115(2)
N(2)–Pb–O(4)	83.7(6)	C(7)–N(4)–C(8)	117(3)
N(3)–Pb–N(4)	70.7(5)	O(1)–N(5)–O(2)	118(2)
N(3)–Pb–O(1)	164.1(6)	O(1)–N(5)–O(3)	122(3)
N(3)–Pb–O(4)	88.3(7)	O(2)–N(5)–O(3)	120(3)
N(4)–Pb–O(1)	101.6(7)	O(4)–N(6)–O(5)	119(2)
N(4)–Pb–O(4)	124.5(6)	O(4)–N(6)–O(6)	121(2)
O(1)–Pb–O(4)	107.2(8)	O(5)–N(6)–O(6)	120(2)
C(1)–N(1)–Pb	107(2)	N(5)–O(1)–Pb	104(2)
C(10)–N(1)–Pb	113(1)	N(6)–O(4)–Pb	103(1)
C(1)–N(1)–C(10)	112(2)	N(1)–C(1)–C(2)	109(3)
C(1)–C(2)–N(2)	109(3)	C(6)–C(7)–N(4)	109(2)
N(2)–C(3)–C(4)	121(4)	N(4)–C(8)–C(9)	115(3)
C(3)–C(4)–C(5)	120(3)	C(8)–C(9)–C(10)	116(3)
C(4)–C(5)–N(3)	114(2)	C(9)–C(10)–N(1)	110(2)
N(3)–C(6)–C(7)	110(2)		

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

complexation in water.[17] However, we find that a complex between L_a and $Pb[NO_3]_2$ is readily formed in dry dmso. It appears that any moisture present during the preparation produces an insoluble white powder, possibly a hydroxo-compound, which may account for the previous failure. The complex is extremely soluble in dmso, in which it is a 2 : 1 electrolyte. It may be isolated as a white crystalline compound whose i.r. spectrum indicates the presence of co-ordinated nitrate ions, in contrast to the behaviour in dmso solution.

Variable-temperature, proton-decoupled, ^{13}C n.m.r. spectra in $[^2H_6]$dmso are shown in Figure 1. At 303 K five resonances of equal intensity are observed, while the peak at 49.3 p.p.m. also shows minor side bands due to coupling to the 24% of the spin ½ nucleus ^{207}Pb, $^2J(^{207}Pb-^{13}C) = 21.3$ Hz. This spectrum clearly implies a folded geometry for the macrocycle and it is qualitatively similar to that of the complex *cis*-$[Rh(L_a)Cl_2]Cl$,[18] where a *cis* folding has been established.[5] Elevated-temperature spectra show the presence of a reversible dynamic conformational process which causes the set of four resonances in the low-field region (45—55 p.p.m.) to collapse to give two lines at 433 K, the outer and inner pairs collapsing together. A complete lineshape analysis of this process [19] gives activation parameters at 298 K of $\Delta H^\ddagger = 110 \pm 10$ kJ mol^{-1} and $\Delta S^\ddagger = 105 \pm 20$ J K^{-1} mol^{-1} and a rate constant $10^2 k_{ex} = 6.2 \pm 1.5$ s^{-1}. Comparison with the parameters of a Berry-type rearrangement in an analogous trigonal-bipyramidal complex $[Zn(L_b)Cl][ClO_4]$ ($\Delta H^\ddagger = 59 \pm 3$ kJ mol^{-1}, $\Delta S^\ddagger = 15 \pm 12$ J K^{-1} mol^{-1}) [9] shows no similarity. Interpretation of the present system as having a macrocycle folded to a trigonal-bipyramidal geometry (nitrogen configurations *R,S,R,S*) is therefore unlikely. The ground-state conformation of the complex is best envisaged as *cis* octahedral with the nitrogen atoms in (*R,R,R,R*) [2,4] or (*S,S,S,S*) configurations (Figure 2).

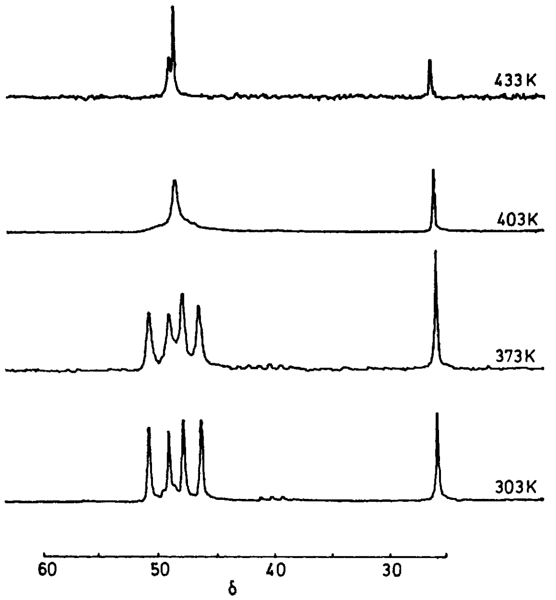

FIGURE 1 Variable-temperature ^{13}C n.m.r. spectra of $[Pb(L_a)][NO_3]_2$ in $[^2H_6]$dmso solution (chemical shifts relative to internal dioxan at $\delta = 67.3$)

The dynamic process can then be interpreted as being interconversion of two identical *cis*-octahedral type geometries (configurations $R,R,R,R \longleftrightarrow S,S,S,S$). This may proceed either by four linked nitrogen inversions or (more likely) by passage of the lead(II) ion through the macrocycle ring as illustrated in Figure 2. This latter process allows the fold in the macrocycle to switch between the two pairs of diagonally placed nitrogen atoms (open and closed circles in Figure 2). Thus what were axial donors become equatorial and *vice versa*, such that at the fast-exchange limit (433 K) the averaging of these conformations will give the macrocycle an apparent square-planar geometry and corresponding three-line spectrum (Figure 1). The high positive entropy of activation for the exchange process is reasonable in terms of the proposed mechanism (Figure 2), since re-arrangement to the intermediate *trans*-type conformation can only proceed with the loss of at least one of the co-ordinated solvent molecules.

The very high solubility of the complex in dmso permitted the accumulation of natural-abundance ^{15}N n.m.r. spectra. The spectrum at 300 K has been reported in a preliminary publication [20] and shows the expected two principal resonances of equal intensity from the axial and equatorial nitrogens, at $\delta = -318.8$ and -325.5 relative to $C^2H_3{}^{15}NO_2$ ($\delta = 0$). The ^{207}Pb isotope also gives $^1J(^{207}Pb-^{15}N)$ couplings to both main peaks, producing minor sidebands. These ^1J coupling constants are strikingly different for the two types of nitrogen atom, being 207.5 (centred at -318.8) and 19.8 Hz (-325.5 p.p.m.). Pople and Santry [21] have factorised the contributions to ^1J coupling constants as contact and spin-dipolar. (Orbital contributions may be neglected in the absence of π bonding.) In addition, these workers indicate that the contact interaction is often dominant, and when comparing coupling constants within the same molecule the spin-dipolar contribution may reasonably be regarded as an approximately constant contribution. It is clear, therefore, that in the present case the large difference in the ^1J couplings to axial and equatorial nitrogens may be assumed to be largely a consequence of the contact interaction,[22] although complications may occur due to the lone pair of electrons on the lead(II) atom. The contact contribution to ^1J is directly dependent upon the *s* character of the bond and the value of the *s*-orbital overlap integral.[23] The very different values obtained for couplings to axial

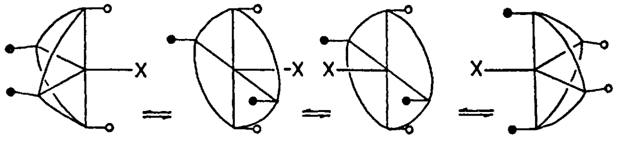

FIGURE 2 Schematic illustration of the possible dynamic process observed in the ^{13}C n.m.r. spectra of $[Pb(L_a)][NO_3]_2$ (closed and open circles represent protons on equivalent nitrogen donors)

and equatorial bonds in this case, therefore, imply very different modes of bonding to the two sites in this molecule.

In order to investigate the origins of these differences an *X*-ray analysis of the complex was performed. The structure is shown in Figure 3 and approximates to the predicted *cis*-octahedral geometry in that it has nitrogen configuration (*R*,*R*,*R*,*R*). However, there is considerable distortion from ideal octahedral geometry in the nitrogen positions (see below), while the *cis*-nitrate groups are also unusual. Each has one shorter Pb–O distance (2.88, 2.96 Å) and one significantly longer (3.08, 3.31 Å) thus showing unsymmetrical bidentate co-ordination,[12] consistent with the i.r. spectrum (although that can only distinguish between the fully symmetrical bidentate geometry and less symmetrical arrangements). Even the shorter Pb–O distances are considerably longer than would be predicted from the Pb–N distances, indicating that the bonding is largely ionic, but raising the problem of why the co-ordination is unsymmetrical. This is normally a response to overcrowding, but here the shortest contact distances [O(2) · · · O(4) 3.24, O(5) · · · N(1) 3.08, O(2) · · · N(2) 3.19 Å] are well above the normal minimum O · · · O of 2.7—2.8 Å.[24] The most reasonable explanation is that the lone pair of the Pb^{II} occupies part of the space between O(1), O(2), O(4), and O(5), although not as much as an individual ligand atom. This may also be partly responsible for the difference between O–Pb and N–Pb distances. The crystal-packing diagram (Figure 4) shows that the forces between the isolated molecules must be mainly H · · · H contacts. A dihedral-angle analysis is given in Table 3 and indicates the macrocycle to be relatively strain-free, except for the C(8)–C(9)–C(10) chelate ring which is somewhat distorted.

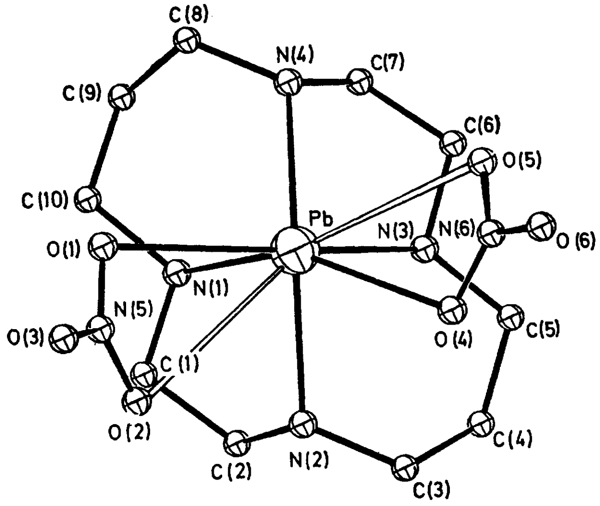

FIGURE 3 Molecular structure of [Pb(L$_a$)][NO$_3$]$_2$

The N–Pb bond lengths of the axial [2.47(2), 2.58(2) Å] and equatorial [2.43(1), 2.47(1) Å] nitrogen atoms show a slight but hardly significant difference in their average values. Such data imply similar bond orders and strengths for the axial and equatorial bonds and so do not mirror the difference in the ^{1}J coupling constants. However, the axial N(2)–Pb–N(4) bond angle of 134.7(6)° shows an enormous distortion from regular octahedral geometry while the equatorial N(1)–Pb–N(3) angle of 83.3(4)° is almost ideal. This distortion is undoubtedly a consequence of the ionic radius of Pb^{II} which prevents the macrocycle from spanning the axial octahedral sites effectively. This means that whereas the equatorial nitrogen atoms are in a favourable position for binding to the hybrid octahedral orbitals of the lead atom, the axial donors are displaced from these ideal positions. This would imply that the axial bonds must either be weaker (not reflected in the bond lengths) or else involve a substantial rehybridisation of the lead(II) orbitals, which could be consistent with the ^{15}N coupling-constant data if it involves a changed *s* character or overlap integral.

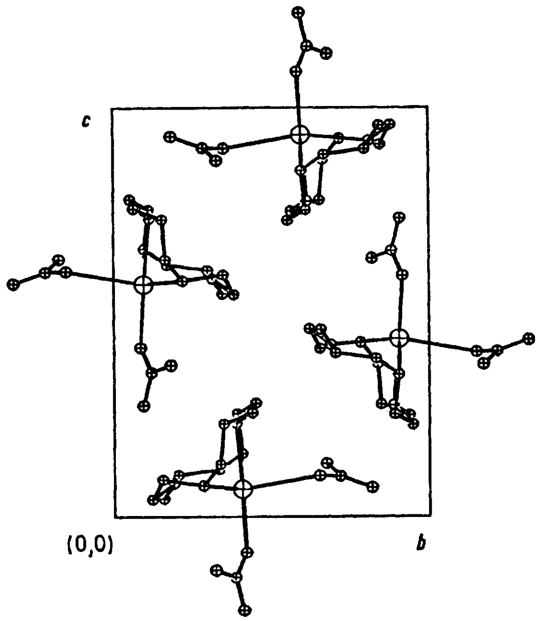

FIGURE 4 Crystal-packing diagram for [Pb(L$_a$)][NO$_3$]$_2$ viewed along the *a* axis

It is proposed, therefore, that if the axial distortion is retained in solution, then the $^{1}J(^{207}Pb-^{15}N)$ values may be assigned as 207.5 Hz for equatorial donors (normal ' octahedral ' hybrid bonds) and 19.8 Hz for axial donors (distorted octahedral bonds). This interpretation ignores the inert pair on the lead(II) atom, which is assumed to affect both coupling constants equally, and implicitly suggests that the value of 207.5 Hz may be

TABLE 3

Dihedral angles (°) with standard deviations in parentheses

C(1)–C(2)–N(2)–C(3)	167(3)	C(6)–C(7)–N(4)–C(8)	37(2)
C(2)–N(2)–C(3)–C(4)	78(4)	C(7)–N(4)–C(8)–C(9)	86(3)
N(2)–C(3)–C(4)–C(5)	56(5)	N(4)–C(8)–C(9)–C(10)	10(1)
C(3)–C(4)–C(5)–N(3)	63(4)	C(8)–C(9)–C(10)–N(1)	48(4)
C(4)–C(5)–N(3)–C(6)	165(2)	C(9)–C(10)–N(1)–C(1)	6(3)
C(5)–N(3)–C(6)–C(7)	176(2)	C(10)–N(1)–C(1)–C(2)	178(2)
N(3)–C(6)–C(7)–N(4)	64(2)	N(1)–C(1)–C(2)–N(2)	60(3)

regarded as 'normal' for a lead–nitrogen bond. Only one previous, indirect, ^{1}J lead–nitrogen value has been reported for the lead(IV) ion (lacking, of course, any 'inert-pair' effect); the ^{1}J value of +261 Hz suggests that the value of 207.5 Hz obtained here is indeed normal. Confirmation comes from another value, recently obtained in these laboratories; $^{1}J(^{207}Pb-^{15}N)$ for the complex $[Pb(cdta)]^{2-}$ has been found to be 188.3 Hz ($cdta^{4-}$ = *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetate ion).

The *cis*-geometry for this complex is the first reported instance of such a geometry with a labile metal ion. The rationalisation of why lead(II) adopts such a geometry in preference to a *trans* geometry is simply that lead(II) is too large to fit within the macrocycle ring. It may well be that, in order to obtain normal lead–nitrogen bond lengths, the macrocycle must fold in the manner described. This implies that a *trans*-(*R*,*S*,*R*,*S*) configuration is impossible because the lead(II) ion, even with this macrocycle conformation, is incapable of sitting at its optimum distance above the four donor atoms.

$[Pb(L_b)][NO_3]_2$.—This complex may be prepared in dry dmso and is extremely soluble in this solvent. It is a 2 : 1 electrolyte and the white solid obtained by removal of the solvent dmso shows a complex i.r. spectrum for the nitrate groups, suggesting that perhaps only one of these is co-ordinated in the solid, in contrast to the behaviour of $[Pb(L_a)][NO_3]_2$ above.

Variable-temperature, proton-decoupled, ^{13}C n.m.r. spectra in $[^{2}H_6]$dmso–$[^{2}H_4]$methanol (4 : 1) are shown in Figure 5. At 330 K the spectrum shows only the four lines expected for a five-co-ordinate *trans* geometry (with *R*,*S*,*R*,*S* nitrogen configurations) exactly as is observed in the case of the zinc(II) complex of L_b.[9] Upon cooling, however, all four resonances begin to broaden, and each eventually splits into an unequal doublet at 260 K. The resulting eight lines may be divided into two sets of four, labelled F and B in the Figure, and those labelled F are readily assigned to free macrocycle. The observed dynamic process is therefore interpreted as being macrocycle exchange between free, F, and bound, B, environments, the latter containing the macrocycle in a *trans*-(*R*,*S*,*R*,*S*) conformation with the lead(II) atom sitting above the macrocycle plane and being apically capped in a square pyramid by a solvent dmso molecule. The stability constant of the complex, estimated from integrals, is *ca.* 1.3 dm^3 mol^{-1} at 260 K, and a complete lineshape analysis of the dynamic process[19] gives activation parameters (298 K) for macrocycle exchange of $\Delta H^{\ddagger} = 38.5 \pm 0.7$ kJ mol^{-1} and $\Delta S^{\ddagger} = -70 \pm 3$ J K^{-1} mol^{-1} with $k_{ex} = 240$ s^{-1}.

The negative activation entropy implies that there is increased solvation in the transition state. This is a reasonable result since any unwinding of the macrocycle from the metal ion must lead to increased solvation of both the lead(II) and the partially unwound macrocycle. This complex is the only one of L_b which we have studied which shows macrocycle exchange on the n.m.r. time scale, complexes with Zn^{II}, Cd^{II}, and Hg^{II} showing no measurable exchange. It is clear that the present complex is unusual, but its low stability and rapid macrocycle exchange may be explained by reference to the structure of $[Pb(L_a)][NO_3]_2$ discussed above. In this latter complex, the lead(II) ion is too big to allow any kind of planar, *trans*-like, co-ordination of the four nitrogen donors and enforces a *cis*-type conformation upon the 14-membered ring. With L_b as the ligand, therefore, the same ring size will again tend towards a *cis* geometry but in this case it has been pointed out[9,13] that the nitrogen configurations of co-ordinated L_b (*R*,*S*,*R*,*S*) are inconsistent with a *cis* geometry (configurations *R*,*R*,*R*,*R* or *S*,*S*,*S*,*S*) and there is no available route for inverting these configurations. The macrocycle is forced, therefore, to adopt a most unfavourable geometry for this very large metal ion (r = 1.21 Å) and, as a consequence, the complex formed is comparatively very unstable.

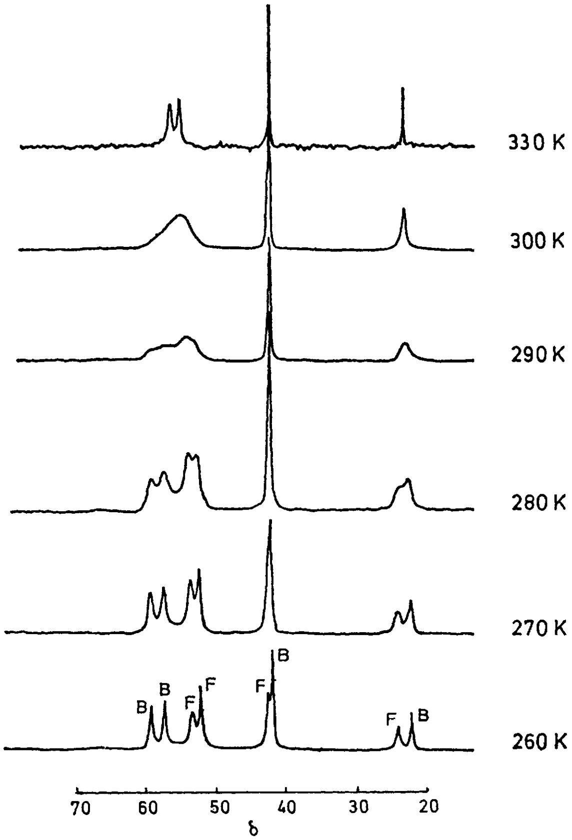

FIGURE 5 Variable-temperature ^{13}C n.m.r. spectra of $[Pb(L_b)][NO_3]_2$ in $[^{2}H_6]$dmso–$[^{2}H_4]$methanol (4 : 1) solution. F and B denote resonances of free and bound macrocycle respectively (chemical shifts relative to internal dioxan at δ = 67.3)

It is also interesting to note that the resonances B of the complexed ligand in Figure 5 do not split further at temperatures down to 233 K, indicating that the complex is not folding to a trigonal bipyramid, as is found for complexes of zinc(II)[9] and all other d^{10} metal ions. This retention of a square-pyramidal geometry is presumably due to the steric requirements of the large lead(II) ion.

Conclusions.—We have previously shown[1] that both metal-ion radius and availability of co-ordination sites can affect the overall geometry of a macrocycle complex with a metal ion. In this case it is found that the geometry and stability are severely affected, not only by the metal-ion size but also by the possible nitrogen-donor-atom configurations. With L_a, where interchange of the configurations of co-ordinated donors is relatively easy, the complex with lead(II) is stable and is *cis*-octahedral (*R*,*R*,*R*,*R* or *S*,*S*,*S*,*S*). With L_b, on the other hand, nitrogen inversion is prohibited and the resulting *trans*-(*R*,*S*,*R*,*S*) complex is unstable with respect to dissociation.

The compounds L_a and L_b also give complexes of unusual stereochemistry with other heavy metal ions, Cd^{II} and Hg^{II}, and their structural and dynamic behaviour will be reported elsewhere.

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