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Structure of (1,4,8,11-tetra-azacyclotetradecane)lead (II) Dinitrate, as Shown by an X-Ray Crystal Structure and by Natural Abundance ^{13}C and ^{15}N N.M.R. in Dimethyl Sulphoxide Solution

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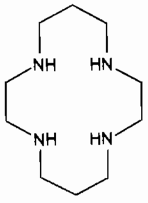
Although transition metal complexes of the macrocyclic ligand 1,4,8,11-tetra-azacyclotetradecane (L) have been known for several years, no complexes with non-transition metals have been characterised. We have, therefore, synthesised the first such complex of (L) with lead(II) as part of our studies on the co-ordination chemistry of heavy metal ion-macrocycle complexes [1]. Previous attempts at this preparation by other workers failed to show any complexation in water [2], but we find that a complex of L with $Pb(NO_3)_2$ is readily formed in dry DMSO. The complex is extremely soluble in DMSO (> 1 mol dm^{-3}) and conductivity measurements with a 2 X 10^{-3} mol dm^{-3} solution shows it to be a 2:1 electrolyte. The white crystalline compound resulting from precipitation with methanol analyses as $Pb(L)(NO_3)_2$. Bosnich *et al.* [3] have shown that there are five possible strain-free octahedral geometries of the ligand L in its complexes, four involving *trans*-square-planar co-ordination, and the fifth a *cis*-folded conformation of the ligand. Only one such *trans*-geometry has been observed in practice, *trans*-III [2, 4], whilst the folded *cis*-geometry has only been found with inert metals such as Co^{III} [5] and Rh^{III} [6]. Consideration of the possible structure of the present complex suggests that the lead(II) ion is too large to be accommodated within the ring in a regular square-planar geometry [7], and so some form of folding of the macrocycle away from planarity may be predicted.



(L)

^{13}C n.m.r. spectra in $^2H_6$-DMSO show five equal intensity resonances for the complex at 300 K (δ = 50.93, 49,24, 48.01, 46.55, 26.11 ppm, ref. dioxan 67.26 ppm), indicating that the ligand is folding about two diagonally placed nitrogen atoms. Elevated temperature (330–430 K) spectra show the presence of a dynamic process which causes the five lines at 300 K to collapse to give three lines in the intensity ratio 2:2:1 at 430 K (δ = 49.06, 48.69, 26.58 ppm ref. dioxan 67.26 ppm). The 300 K spectrum closely resembles that of the complex *cis*-$[Rh(L)Cl_2]Cl$ [6, 8] and this, together with the high energy of activation for the dynamic process ($\Delta G^{\neq}_{298} \simeq 88$ kJ mol^{-1}), strongly suggests that the folding of L has occurred to give a *cis*-octahedral-type geometry. The dynamic process is therefore interpreted as being interconversion of two identical *cis*-octahedral geometries, either by four linked nitrogen inversions or, more likely, by passage of the Pb(II) ion through the macrocycle ring; this allows the fold in the macrocycle to switch between the two equivalent diagonal pairs of nitrogen atoms. At the fast exchanging limit (430 K) the averaging of these conformations would give the macrocycle an apparent square-planar geometry with a corresponding 3 line, 2:2:1, ^{13}C spectrum, as observed.

The very high solubility of the complex in DMSO allowed the recording of natural abundance ^{15}N n.m.r. spectra, and the splitting due to the 21% of the spin $\frac{1}{2}$ isotope, ^{207}Pb, enabled us to directly measure the lead–nitrogen ^1J coupling constants. The 300 K spectrum, Fig. 1, confirms the corresponding ^{13}C spectrum, showing two resonances, one each for the axial and equatorial nitrogens, and each has associated side bands due to the one-bond metal–N coupling. However, the $^1J(^{207}Pb–^{15}N)$ coupling constants are surprisingly different for the two types of nitrogen present, being 207.5 and 19.8 Hz. This implies very different modes of bonding for the axial and equatorial sites of this complex [9].

We have determined the X-ray crystal structure of the complex to examine this further.

Crystal Data

$C_{10}H_{24}N_6O_6Pb$, *M* 531.2; monoclinic, space group *P*2$_1$/*c*, *a* = 10.326(2), *b* = 11.145(3), *c* = 14.832(4) Å, β = 96.19(2), *U* = 1697.0(7) Å^3, *Z* = 4, D_c = 2.08 g cm^{-3}, μ(MoKα) = 100.61 cm^{-1}. 1909 out of 3360 reflections (Syntex $P2_1$ diffractometer) measured to $2\theta = 50°$ (MoKα radiation, 18 ± 2 °C) were retained ($I \geqslant 3.0$) and used to solve the structure by conventional Patterson and Fourier techniques to give an R-factor of 0.049.

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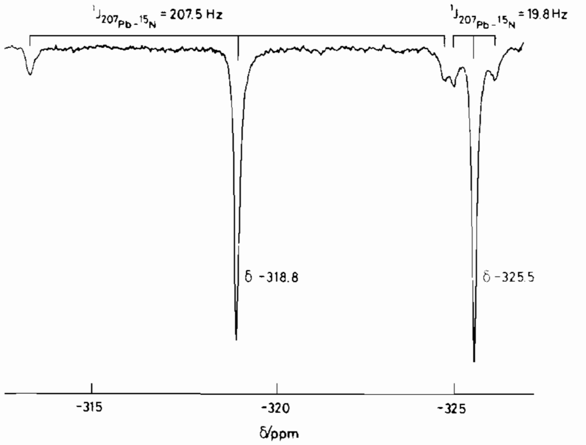

Fig. 1. Natural abundance ^{15}N n.m.r. spectrum of *cis*-[Pb-(L)-(DMSO)$_2$]$^{2+}$ ion in [^{2}H]$_6$-DMSO at 300 K, showing ^{1}J(^{207}Pb–^{15}N) couplings (shifts referenced to external $C^2H_3{}^{15}NO_2$ at $\delta = 0$ ppm). Spectrum recorded with a Bruker WH180 spectrometer, 25 mm diameter tube, 0.9 mol dm^{-3}, 20,339 scans. δ, NO_3^- ion = –11.75 ppm.

The two nitrate ions are co-ordinated in a monodentate fashion, and the complex (Figure 2) approximates to the predicted octahedral *cis*-geometry, but with some distortion even though the lone-pair of electrons on the lead(II) ion appears to be stereochemically inactive. Dihedral angle analysis indicates the macrocycle to be nearly strain-free, while the metal–nitrogen bond lengths for axial (2.47(2), 2.58(2) Å) and equatorial (2.43(1), 2.47(1) Å) donors show slight lengthening, on average, of the axial bonds, but no marked difference as might have been expected from the ^{1}J(^{207}Pb–^{15}N) coupling constant data. However, the axial N–Pb–N bond angle of 135° illustrates a considerable distortion from regular octahedral geometry. This is undoubtedly a consequence of the large Pb(II) ionic radius which prevents the macrocycle from spanning the axial octahedral sites effectively. This means that whereas the equatorial nitrogen atoms are in a favourable orientation for co-ordination and may be expected to form relatively normal bonds to lead(II), the axial donors are displaced from their most favourable positions for binding to the hybrid d^2sp^3 octahedral orbitals of the lead atom. This would imply that these latter Pb–N bonds must either be weaker, which is not evident from the bond lengths, or involve a substantial rehybridisation of the lead orbitals, which, if this meant considerably less *s*-character or a smaller *s*-overlap integral [9] in the new bonding hybrids, would be consistent with the ^{15}N coupling constant data (ignoring spin–dipolar contributions to the coupling constants [9]).

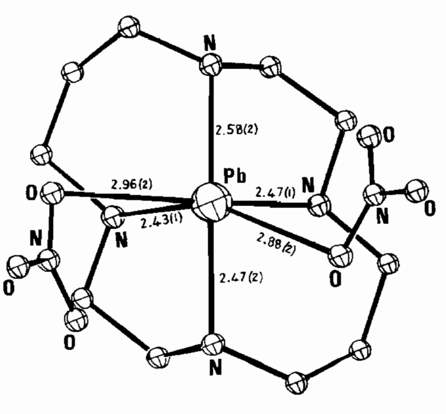

Fig. 2. X-ray structure of *cis*-[Pb(L)(NO$_3$)$_2$]. Unlabelled atoms are carbon. Bond lengths given in Å.

Therefore, we suggest that if the axial distortion is retained in solution then the ^{1}J(^{207}Pb–^{15}N) values can be assigned as 207.5 Hz for the "equatorial" nitrogen atoms ("normal" octahedral hybridisation) and 19.8 Hz for the "axial" nitrogen atoms (distorted octahedral rehybridisation involving less *s*-character or smaller *s*-overlap). One other ^{1}J(^{207}Pb–^{15}N) coupling constant has been reported previously [10]; by using 95% ^{15}N-enriched material and ^{1}H{^{207}Pb} double resonance, a value of 261 Hz was recorded for Me_3-PbNMePh, and this value is similar to that assigned to the relatively unstrained "equatorial" Pb–N bonds. It is clearly desirable to obtain many more ^{1}J metal–nitrogen coupling constants in order to confirm these assignments, and to explore their dependence on metal hybridisation. This work is now in progress.

Acknowledgments

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