

Intramolecular Exchange between Square Antiprismatic Enantiomers of the Pendant Arm Macrocyclic Ligand Complex *N,N',N'',N'''*-Tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecanelead(II)

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Variable temperature ¹³C NMR studies of the pendant arm macrocyclic complex *N,N',N'',N'''*-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecanelead(II) and its cadmium(II) and mercury(II) analogues in [²H₄]-methanol indicate that these complexes undergo rapid intramolecular exchange between two square antiprismatic enantiomers.

The substitution of coordinating pendant arms on to polyaza macrocyclic ligands may have two interesting effects on metal ion complexation. The first is that initial metal ion capture by the pendant arms may accelerate the entry of metal ions into the macrocyclic cavity (and thereby render such ligands suitable for metal ion scavenging in industrial applications).¹⁻³ The second, and less studied, effect is that the increased denticity of the pendant arm polyaza macrocyclic ligand generates possibilities for stereochemistries and intramolecular processes in its metal complexes which are not available to the complexes formed by the parent ligand.^{4,5} It is this second effect, which results in the unusual observation of rapid intramolecular exchange between enantiomers in the octadentate pendant arm macrocyclic complex *N,N',N'',N'''*-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclotetradecanelead(II), [Pb(thecl2)]²⁺, and its cadmium(II) and mercury(II) analogues, which is explored here.

We have observed the temperature dependent coalescence of the ¹³C NMR spectrum of [Pb(thecl2)]²⁺ (Fig. 1) in [²H₄]methanol from which it is possible to assign both a structure to the complex and a mechanism to the intramolecular exchange process causing the spectral coalescence. The slow exchange spectrum of [Pb(thecl2)]²⁺ consists of a pair of resonances at high field which coalesce to a single resonance as the temperature is increased and which are assigned to the macrocycle carbons, and a pair of resonances at low field which does not coalesce as the temperature is increased and which is assigned to the 2-hydroxyethyl arm carbons. This is consistent with the intramolecular exchange of [Pb(thecl2)]²⁺ between two square antiprismatic enantiomers of C₄ symmetry in which lead(II) is coordinated by the four nitrogens of the macrocycle and the hydroxy groups of the four 2-hydroxyethyl arms of thecl2 through the mechanism shown in Fig. 2. {The observation of enantiomeric approxi-

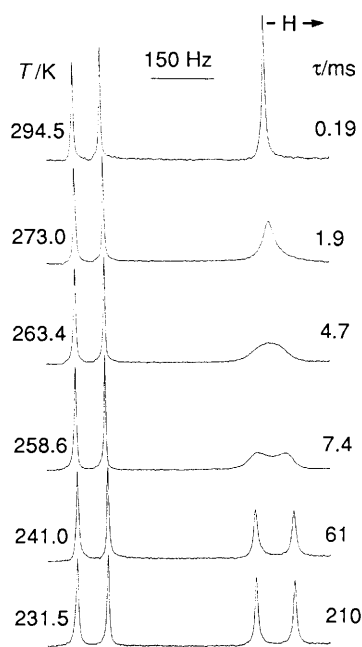


Fig. 1 A selection of ^{13}C 75.47 MHz NMR spectra of $[\text{Pb}(\text{thecl}_2)]^{2+}$ (0.03 mol dm^{-3}) in $[\text{2H}_4]$ -methanol at different temperatures. The site lifetimes, τ , values were derived from complete lineshape analyses of the exchange modified high field resonances arising from the macrocyclic ring carbons. The broadening of the low field resonances arising from the 2-hydroxyethyl pendant arms is a consequence of the increase in solution viscosity with decrease in temperature.

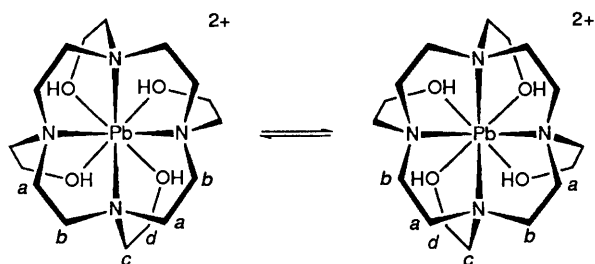


Fig. 2 Proposed mechanism for the interconversion of the square antiprismatic enantiomers of $[\text{Pb}(\text{thecl}_2)]^{2+}$ viewed from above the tetraaza macrocyclic plane

mately square antiprismatic structures for $[\text{K}(\text{thecl}_2)]^+$ in the solid state^{6,7} provides support for this mechanism which does not require perfect antiprismatic stereochemistry. It is seen that the macrocyclic carbons are exchanged between the inequivalent sites (*a*) and (*b*) whereas the 2-hydroxyethyl carbons, (*c*) and (*d*), experience no change in magnetic environment when the enantiomers interconvert. Thus coalescence is observed for the macrocycle resonances, but not for the resonances arising from the 2-hydroxyethyl pendant arms.

The mean site lifetime (τ/ms) for the macrocyclic carbons in sites (*a*) and (*b*), derived from a complete lineshape analysis of the coalescence of their resonances,⁸ and the corresponding temperatures (*K*), shown in parentheses, are: 210 (231.5), 110 (236.0), 61 (241.0), 20 (249.6), 12 (254.1), 7.4 (258.6), 4.7 (263.4), 2.6 (268.1), 1.9 (273.0), 0.76 (281.0), 0.48 (285.0), 0.32 (289.5) and 0.19 (294.5). A fit of these data to eqn. (1) yields the kinetic parameters: k (298.2 K) = $(6.55 \pm 0.26) \times 10^3 \text{ s}^{-1}$, $\Delta H^\ddagger = 60.4 \pm 0.7 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 30.6 \pm 2.8 \text{ J K}^{-1} \text{ mol}^{-1}$. If all eight thecl2 donor atoms remain coordinated in the transition state its geometry will be square prismatic, and ΔH^\ddagger and ΔS^\ddagger represent the differences between the square antiprismatic and prismatic geometries for $[\text{Pb}(\text{thecl}_2)]^{2+}$. The moderately high ΔH^\ddagger is consistent with a combination of a lengthening of the metal to ligand bonds and

an increase in steric hindrance in the square prismatic transition state, and the positive ΔS^\ddagger is indicative of the concomitant decrease in order. However, the possibility that one or more 2-hydroxyethyl arms becomes monodentate in the transition state cannot be ruled out at this stage, and such a transition state could also account for the observed ΔH^\ddagger and ΔS^\ddagger values.

$$1/\tau = k = (k_B T/h) e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (1)$$

At 298.2 K the ^{13}C NMR spectra of $[\text{Cd}(\text{thecl}_2)]^{2+}$ and $[\text{Hg}(\text{thecl}_2)]^{2+}$ in $[\text{2H}_4]$ -methanol are also characterised by two low field resonances arising from the 2-hydroxyethyl arms and a high field singlet arising from the carbons of the macrocycle similar to those observed for the fast exchange limiting spectrum of $[\text{Pb}(\text{thecl}_2)]^{2+}$, and also consistent with the operation of an intramolecular exchange process similar to that in Fig. 2. Although broadening of the high field resonance of $[\text{Cd}(\text{thecl}_2)]^{2+}$ occurred as temperature was decreased, unequivocal observation of the emergence of the two resonances expected for the slow exchange limiting spectrum was obscured as the decrease in the chemical shift difference between the broadening high field resonance and the $[\text{2H}_4]$ -methanol multiplet resonance with temperature led to their superimposition in the critical temperature range 180–210 K. Broadening of the single high field resonance of $[\text{Hg}(\text{thecl}_2)]^{2+}$ occurred at 250 K and below 230 K it appeared to resolve into two resonances, but that at higher field was partly obscured by the $[\text{2H}_4]$ -methanol multiplet resonance so that only the estimate k (210 K) $\sim 10 \text{ s}^{-1}$ ($\tau \sim 100 \text{ ms}$) was obtained.

The eight-coordination of the pendant arm macrocyclic ligand in $[\text{M}(\text{thecl}_2)]^{2+}$ ($\text{M}^{2+} = \text{Cd}^{2+}$, Hg^{2+} and Pb^{2+}) contrasts with the six-coordination of N, N', N'', N''' -tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane (thecl4) in $[\text{M}(\text{thecl}_4)]^{2+}$ ($\text{M}^{2+} = \text{Cd}^{2+}$, Hg^{2+} and Pb^{2+}). ^{13}C NMR studies of the latter complexes in $[\text{2H}_4]$ -methanol are consistent with M^{2+} being coordinated by four nitrogens and two oxygens in a trigonal prismatic stereochemistry with the macrocycle in the *trans* III configuration.^{2,4,5} These data from the twelve and fourteen membered pendant arm macrocyclic $[\text{M}(\text{thecl}_2)]^{2+}$ and $[\text{M}(\text{thecl}_4)]^{2+}$ indicate the importance of the configuration of the macrocycle ring and the orientation of the 2-hydroxyethyl pendant arms in determining complex stereochemistry and the consequent possibilities for intramolecular rearrangements. These stereochemical aspects may also impinge on the rate of entry of the metal ion into the macrocyclic cavities of pendant arm ligands in complex formation.

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