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Transannular Oscillation of Metal Centers in the Pendant Arm Macrocyclic Complex [1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane]mercury(II) and Its Lead(II) Analogue. NMR Study of the ^{13}C Natural Abundance and Specifically Enriched Complexes

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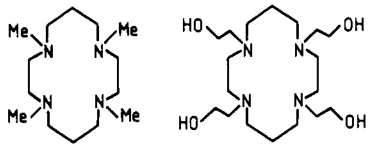
A ^{13}C NMR study of [1,4,8,11-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane]mercury(II) and its lead(II) analogue, [M(THEC)]$^{2+}$ (M = Hg, Pb), in CD$_3$OD, shows that the most probable structure of these complexes in solution incorporates the 1,4,8,11-tetraazacyclotetradecane ring in the trans III configuration with the metal center above the tetraaza plane and trigonal-prismatically coordinated by four ring nitrogens and two hydroxyethyl pendant arms attached to either end of the same 1,3-diaminopropane moiety. Dynamic ^{13}C NMR studies of [M(THEC)]$^{2+}$ are consistent with a rapid pairwise intramolecular exchange of the hydroxyethyl arms between mono- and bidentate coordination simultaneously with the oscillation of M(II) through the macrocyclic annulus of THEC. This pairwise exchange of the hydroxyethyl arms is characterized by $k(298.2\ \mathrm{K}) = 3130 \pm 120$ and $11\,220 \pm 200\ \mathrm{s}^{-1}$, $\Delta H^{\ddagger} = 38.0 \pm 0.6$ and $45.4 \pm 0.3\ \mathrm{kJ\ mol}^{-1}$, and $\Delta S^{\ddagger} = -50.6 \pm 2.1$ and $-15.2 \pm 1.1\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$, respectively, for M = Hg and Pb.

The current interest in selective metal ion complexation has resulted in studies which show that the metal complexes formed with pendant arm polyaza-macrocyclic ligands exhibit a considerable variation in stability, lability, and structure as the size of the macrocycle, and the nature of the metal ion and the pendant arm, is varied.[1-9] We are particularly interested in the solution characteristics of heavy-metal complexes formed by 1,4,8,11-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane, THEC, as a consequence of our recent study of [Cd(THEC)]$^{2+}$, which revealed unusual structural and intramolecular exchange characteristics.[1] Solution and solid-state ^{13}C NMR spectra showed that the most probable structure of [Cd(THEC)]$^{2+}$ incorporates the 1,4,8,11-tetraazacyclotetradecane ring in the trans III configuration with the metal center above the tetraaza plane and trigonal-prismatically coordinated by four ring nitrogens and two hydroxyethyl pendant arms attached to either end of the same 1,3-diaminopropane moiety.[1] The temperature variation of the natural abundance and specifically enriched ^{13}C NMR spectra of [Cd(THEC)]$^{2+}$ were consistent with a rapid pairwise intramolecular exchange of the hydroxyethyl arms occurring simultaneously with a rapid oscillation of Cd(II) through the macrocyclic annulus of THEC. The uncommon structure of [Cd(THEC)]$^{2+}$ and the operation of the unusual intramolecular process have prompted us to investigate the structure and intramolecular exchange processes of [Hg(THEC)]$^{2+}$ and [Pb(THEC)]$^{2+}$.



TMC THEC

Experimental Section

Synthesis of [1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane]mercury(II) Perchlorate and Its Lead(II) Analogue. 1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane (THEC) was prepared and purified according to literature methods.[2] ^{13}C enrichment of all of the hydroxyethyl arm methylene groups of THEC was achieved by using 99 atom % ^{13}C$_2$-enriched ethylene oxide (Cambridge Isotope Laboratories) in place of unenriched ethylene oxide. [Pb(THEC)](ClO$_4$)$_2$ was prepared (yield 92%) in a similar manner to that previously described for [Cd(THEC)](ClO$_4$)$_2$.[1] Anal. Calcd for C$_{18}$H$_{40}$Cl$_2$N$_4$O$_{12}$Pb: C, 27.6; H, 5.2; N, 7.2. Found: C, 27.9; H, 4.9; N, 7.0. IR (Nujol): 3425 cm^{-1}, br ($\nu_{\mathrm{O-H}}$). Λ_{M}: 57 cm^2 Ω^{-1} mol^{-1} (DMSO) (1:2).[10]

[Hg(THEC)](ClO$_4$)$_2$ is less stable than its Cd(II) and Pb(II) analogues, and this necessitates a different preparative procedure. A solution of THEC (0.01 g, 0.26 mmol) in absolute ethanol (5 cm^3), kept under dry argon, was cooled to 268 K. Triaquamercury(II) perchlorate (0.12 g, 0.26 mmol) was added and the resulting suspension stirred for 30 min. The white microcrystalline product was collected by filtration, washed with cold (268 K) absolute ethanol (1 × 5 cm^3), and dried under vacuum (yield 0.16 g, 78%). When stored at 260 K in the dark under argon, [Hg(THEC)](ClO$_4$)$_2$ is stable for several weeks. Anal. Calcd for C$_{18}$H$_{40}$Cl$_2$HgN$_4$O$_{12}$: C, 27.8; H, 5.2; N, 7.2. Found: C, 27.4; H, 5.2; N, 7.1. IR (Nujol): 3425 cm^{-1}, br ($\nu_{\mathrm{O-H}}$). Λ_{M}: 144 cm^2 Ω^{-1} mol^{-1} (MeOH) (1:2).[10]

Elemental analyses were performed by the Australian Microanalytical Service, Infrared spectra were recorded on a Perkin Elmer 297 spectrometer. Conductivity measurements were made on 10^{-3} mol cm^{-3} solutions at 293.2 K by using a Phillips PW9504 conductivity bridge.

NMR Spectroscopy. ^{13}C (75.47 MHz) spectra were run on a Bruker CXP-300 spectrometer locked on deuterium. Solutions of the complexes were prepared under an atmosphere of argon by using CD$_3$OD, which had been dried over Linde 3-Å molecular sieves. For each solution an average of 6000 transients were accumulated in a 2048-point data base at temperature intervals of ca. 5 K. Sweep widths of 5000 and 2500 Hz were employed for the natural abundance and ^{13}C-enriched spectra, respectively, with a recycle time of 1.2 s. Sample temperature was controlled by a Bruker B-VT1000 variable-temperature unit to within ±0.3 K. Temperature calibration in the presence of broad-band proton decoupling was carried out as described in the literature.[11,12] The Fourier transformed spectra were subjected to complete line-shape analysis on a VAX 11780 computer using a density matrix method similar to that

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† University of Adelaide.
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described elswhere.[13-15] The temperature dependences of chemical shifts and line widths in the absence of chemical exchange required in the line-shape analysis were extrapolated from low-temperature spectra where the rate of exchange was slow on the NMR time scale. ^{13}C chemical shifts were referenced to internal CD_3OD assigned a chemical shift of 47.05 ppm.[16]

The CPMAS ^{13}C spectra of solid-state [M(THEC)]$(ClO_4)_2$ were obtained with standard procedures. Chemical shifts were referenced to the low-field resonance of external adamantane, which was assigned a chemical shift of 38.23 ppm.

Results and Discussion

Natural Abundance Solution ^{13}C NMR Spectra. At 297.8 K a CD_3OD solution containing free THEC (0.030 mol dm^{-3}) and [Hg(THEC)]$^{2+}$ (0.020 mol dm^{-3}) exhibits two sets of natural abundance ^{13}C resonances, each of intensity ratio 2:2:2:2:1, at 58.16, 54.38, 51.00, 49.12, and 23.39 ppm arising from THEC and 59.16, 56.88, 56.33, 51.41, and 22.84 ppm arising from [Hg(THEC)]$^{2+}$. By comparison with the spectrum of ^{13}C-enriched THEC, the ^{13}C natural abundance THEC resonances at 58.16 and 54.38 ppm are assigned to the hydroxyethyl arm carbons, that at 23.39 ppm is assigned to the 1,3-diaminopropane medial carbons, and the remaining two resonances are assigned to the 1,2-diaminoethane moieties and the $-NCH_2-$ carbons of the 1,3-diaminopropane moieties. In a similar manner the resonances of [Hg(THEC)]$^{2+}$ at 56.88 and 56.33 ppm are assigned to the hydroxyethyl arom carbons, that at 22.84 ppm is assigned to the 1,3-diaminopropane medial carbons, and the remaining two resonances are assigned to the 1,2-diaminoethane moiety and the $-NCH_2-$ carbons of the 1,3-diaminopropane moieties. Similarly the spectra of THEC and [Pb(THEC)]$^{2+}$ (0.030 and 0.020 mol dm^{-3}, respectively, in CD_3OD solution at 276.5 K) exhibit a set of five resonances of intensity ratio 2:2:2:2:1 at 58.24, 54.42, 51.03, 49.14, and 23.48 ppm and a set of four resonances of intensity ratio 2:4:2:1 at 57.56, 56.21 (two superimposed resonances), 51.94, and 23.05 ppm, respectively. The THEC resonances are assigned in the same chemical shift sequence as for THEC in the presence of [Hg(THEC)]$^{2+}$ in the first solution. The differences in the chemical shifts of the THEC resonances between the two solutions are attributable to temperature and concentration differences and the onset of intermolecular THEC exchange in [Pb(THEC)]$^{2+}$. The resonances of [Pb(THEC)]$^{2+}$ at 57.56 and 56.21 ppm are assigned to the hydroxyethyl arm carbons, that at 23.05 ppm is assigned to the 1,3-diaminopropane medial carbons, and the remaining two resonances are assigned to the 1,2-diaminoethane moieties and the $-NCH_2-$ carbons of the 1,3-diaminopropane moieties.

The observation of separate spectra showing no broadening for THEC and [Hg(THEC)]$^{2+}$ indicates that intermolecular ligand exchange is in the very slow exchange regime of the NMR time scale, and an upper limit for the intermolecular rate constant for exchange of THEC on [Hg(THEC)]$^{2+}$, k_M, may be obtained through eq 1, where $W_{1/2\mathrm{obs}}$ is the observed width (Hz) of the

$$1.5\pi W_{1/2\,\mathrm{obs}} - \pi W_{1/2\,\mathrm{obs}} = 1/\tau_M = X_L/(\tau_L X_M) = k_M \qquad (1)$$

[Hg(THEC)]$^{2+}$ resonance at half-amplitude, $1.5W_{1/2\,\mathrm{obs}}$ is the width that would be observed if the rate of intermolecular exchange was sufficient to increase the natural line width by half, X_M and X_L are the mole fractions of THEC in [Hg(THEC)]$^{2+}$ and the free state, and τ_M and τ_L are the corresponding mean lifetimes. The $W_{1/2\,\mathrm{obs}}$ values range from 5.0 to 9.0 Hz and the upper limit of k_M(293.0 K) = 8–15 s^{-1}, calculated through eq 1. Both sets of resonances arising from the solution containing THEC and [Pb(THEC)]$^{2+}$ are broadened as a consequence of intermolecular ligand exchange and, in the latter case, as a consequence of intramolecular exchange also for the resonances at 57.56, 51.94, and 23.05 ppm (as is discussed in detail below). The [Pb(THEC)]$^{2+}$ resonance at 56.21 ppm arises from the superimposition of two resonances broadened and shifted as a consequence of intermolecular THEC exchange. Because the THEC resonances only broadened by ca. 5 Hz (by comparison with $W_{1/2\,\mathrm{obs}}$ of ca. 5 Hz characterizing the narrower resonances of THEC in a solution containing THEC alone) due to intermolecular exchange processes, the calculation of the rate constant for intermolecular exchange of THEC on [Pb(THEC)]$^{2+}$, k_M(276.5 K) = ca. 25 s^{-1}, was based on these resonances by using an equation analogous to eq 1.

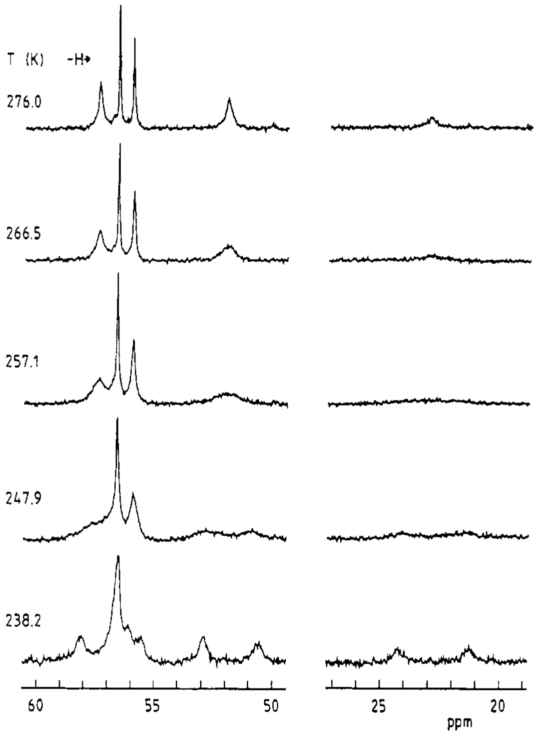

Figure 1. Temperature variation of ^{13}C 75.47-MHz broad-band proton-decoupled NMR spectra of [Hg(THEC)]$^{2+}$ (0.020 mol dm^{-3}) in CD_3OD.

The free THEC spectrum retains its five resonances as temperature is decreased, while each of the [Hg(THEC)]$^{2+}$ resonances splits into two resonances of similar intensity at 218.2 K, as seen in Figure 1 (partial superimposition of resonances occurs at 54–56 ppm). This reversible coalescence phenomenon is consistent with each carbon exchanging intramolecularly between two inequivalent sites as Hg(II) exchanges between two equivalent sites in [Hg(THEC)]$^{2+}$. The [Hg(THEC)]$^{2+}$ pattern of five pairs of resonances requires the two 1,3-diaminopropane moieties to be inequivalent with the two inequivalent medial carbons being within the same plane of symmetry, or on a C_2 axis, characterizing the [Hg(THEC)]$^{2+}$ structure. A very similar coalescence pattern of 10 resonances has also been observed for [Cd(THEC)]$^{2+}$.[1]

Only eight resonances are resolved in the slow intramolecular exchange spectrum of [Pb(THEC)]$^{2+}$ (Figure 2) at 238.2 K, but the spectral intensities suggest that five pairs of resonances are present in the spectrum, with resonance superimposition occurring, characterizing a symmetry similar to that discussed for [Hg(THEC)]$^{2+}$. It is seen that for a given temperature the [Pb(THEC)]$^{2+}$ resonance pairs are in different regions of the NMR kinetic time scale, as a consequence of the differing magnitudes of their chemical shift differences (as is also the case for [Hg(THEC)]$^{2+}$). At lower temperatures the [Pb(THEC)]$^{2+}$ resonances become broader consistent with an increase in solution viscosity.

Solution Structure of [M(THEC)]$^{2+}$ and Intramolecular Exchange Processes. It is necessary to deduce the structure of [M(THEC)]$^{2+}$ in solution before the ^{13}C NMR spectral coalescences shown in Figures 1 and 2 can be interpreted in terms of an intramolecular exchange process occurring in [M(THEC)]$^{2+}$. A pattern of 10 resonances (Figure 1) requires the medial carbons

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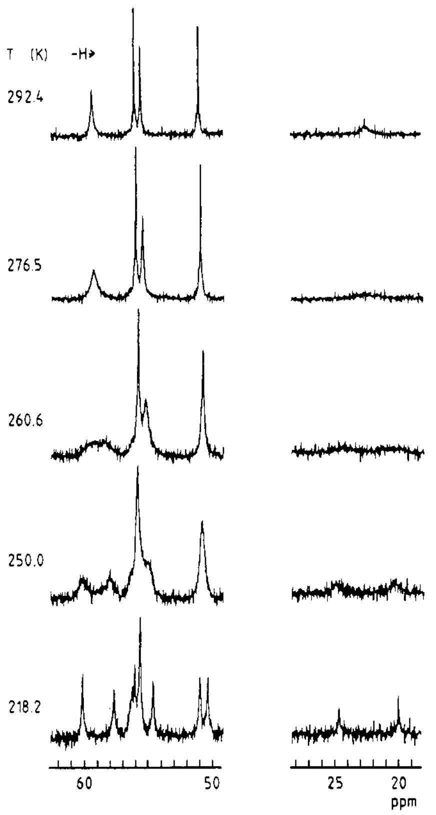

Figure 2. Temperature variation of ^{13}C 75.47-MHz broad-band proton-decoupled NMR spectra of $[Pb(THEC)]^{2+}$ (0.019 mol dm^{-3}) in CD_3OD.

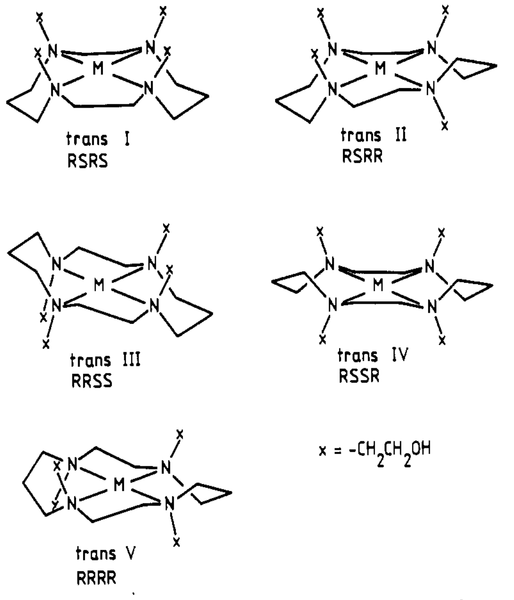

Figure 3. Possible configurational isomers of $[M(THEC)]^{2+}$ in which the hydroxyethyl arms are shown uncoordinated.

of the two 1,3-diaminopropane moieties to be inequivalent but within the same plane of symmetry or on a C_2 axis. Such structures require M(II) to be coordinated by the four coplanar nitrogens of the tetraaza ring and the two hydroxyethyl arms at either end of the same 1,3-diaminopropane moiety. The five possible configurations for the THEC 1,4,8,11-tetraazacyclotetradecane ring with four coplanar nitrogens are trans I–V (Figure 3). The choice of trans III as the most probable configuration of the tetraaza ring has been discussed in detail for $[Cd(THEC)]^{2+}$, and as the same arguments apply for the Hg(II) and Pb(II) analogues, they are reiterated here in abbreviated form only. Thus, the trans II configuration is eliminated as it incorporates 18 inequivalent carbons, which would result in 18 ^{13}C resonances. The trans IV and V configurations both incorporate the unstable skew-boat configuration for the six-membered chelate rings formed by coordination of the 1,3-propanediamine moiety to M(II) and are accordingly considered unlikely configurations for $[M(THEC)]^{2+}$. The trans I configuration, in which all four hydroxyethyl arms are on the same side of the tetraaza plane, provides for the required pairwise coordination of hydroxyethyl arms attached to the same 1,3-diaminopropane moiety, which would result in a 10-resonance ^{13}C spectrum. However, this configuration should also facilitate coordination of the hydroxyethyl arms attached to the same 1,2-diaminoethane moiety, or to diagonally related nitrogens, both of which would result in medial carbon equivalence. No resonances attributable to either of these isomers are observed (detection level of ca. 5% within the prevailing signal to noise ratio for the natural abundance spectra and detection level of ca. 1% in the ^{13}C-enriched spectra discussed below), and accordingly trans I is discounted as a configuration occurring in significant proportions for $[M(THEC)]^{2+}$ in these systems.

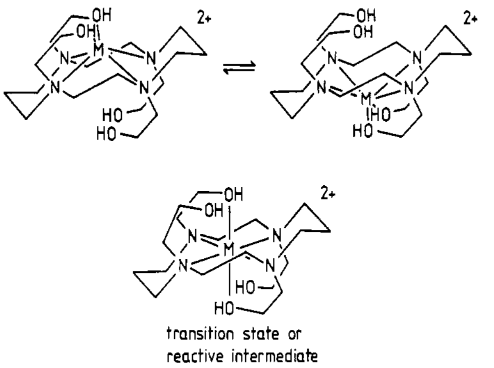

Figure 4. Proposed $[M(THEC)]^{2+}$ structure showing the trans III configuration of THEC and the transannular exchange mechanism.

The observed 10-resonance ^{13}C NMR spectrum and medial inequivalence characterizing $[M(THEC)]^{2+}$ are best accounted for by a structure incorporating the trans III configuration in which M(II) lies above the tetraaza plane and is trigonal-prismatically coordinated by two hydroxyethyl arms and the four ring nitrogens shown in the equivalent structures of Figure 4. (In $[Ni(THEC^*)]^+$, where THEC* is monodeprotonated THEC, the ligand conformation is trans III, as is also the case in $[CuL]^{2+}$, where L = the 14-membered ring macrocyclic ligand 1,4,8,11-tetrakis((hydroxyformyl)methyl)-1,4,8,11-tetraazacyclotetradecane).[3,8]

The simplest mechanism for intramolecular exchange of the medial carbons and the intramolecular pairwise exchange of the other carbons of $[M(THEC)]^{2+}$ appears to be the transannular oscillation of M(II) shown in Figure 4, which has previously been proposed for $[Cd(THEC)]^{2+}$.[1] The transition state, or reactive intermediate, is envisaged to have M(II) in the plane of the tetraaza ring octahedrally coordinated by four nitrogens and two hydroxyethyl arms, one each from either side of the macrocyclic plane. This structure is similar to that observed[3] in the solid state for the Ni(II) complex of deprotonated THEC in which the tetraaza ring is in the trans III configuration with Ni(II) octahedrally coordinated by four nitrogens in the tetraaza plane and two hydroxyethyl arms, one each from either side of the macrocyclic plane and attached to diagonally related nitrogens in a manner similar to that shown in Figure 4. The difference between this structure and that proposed for ground-state $[M(THEC)]^{2+}$ probably arises from the ionic radii[17] of M = Cd, Hg, and Pb (95, 102, and 119 pm, respectively) being substantially greater than that of Ni(II) (69 pm) such that the latter metal ion is more readily accommodated by the macrocyclic hole of THEC. The kinetic parameters derived from the coalescence of the medial

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Table I. Kinetic Parameters for $[M(THEC)]^{2+}$ Intramolecular Exchange Processes Derived from ^{13}C NMR Studies in CD_3OD

M	k(250.0 K), s^{-1}	k(298.2 K), s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
Cd[a,b]	940 ± 20	34 200 ± 1800	44.0 ± 0.6	−10.6 ± 2.2
Cd[a,c]	760 ± 200	68 000 ± 18 000	46.6 ± 4.5	4 ± 15
Hg[b,d]	137 ± 2	3 130 ± 120	38.0 ± 0.6	−50.6 ± 2.1
Hg[c,d]	353 ± 58	9 500 ± 3000	40.0 ± 4.5	−34.3 ± 17.0
Pb[b,d]	275 ± 3	11 200 ± 220	45.4 ± 0.3	−15.2 ± 1.1
Pb[c,d]	495 ± 90	25 000 ± 10 000	48.3 ± 4.4	1.4 ± 15

[a] Reference 1. [b] Derived from specifically ^{13}C-enriched hydroxyethyl $[M(THEC)]^{2+}$. [c] Natural abundance ^{13}C medial carbon data. [d] This work.

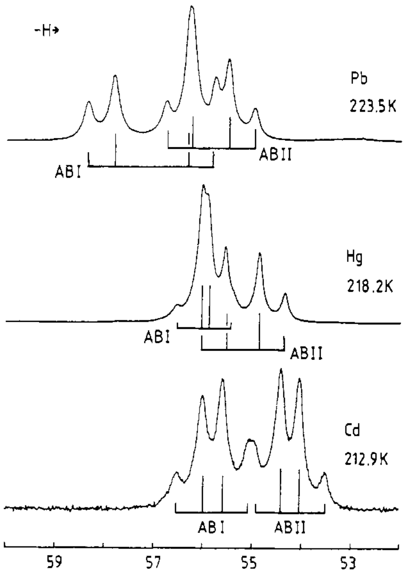

Figure 5. ^{13}C 75.47-MHz NMR spectra of the 99% ^{13}C-enriched hydroxyethyl arms of $[M(THEC)]^{2+}$ in CD_3OD. The individual AB quartets are shown as stick diagrams at the appropriate frequencies, and the heights of the individual lines are proportional to signal intensity. The chemical shifts, δ_A and δ_B (ppm), and coupling constant, J_{AB} (Hz), for each AB quartet are presented in this sequence in parentheses for each quartet: $[Pb(THEC)]^{2+}$ (0.013 mol dm^{-3}), ABI (58.02, 56.06, 40.5), ABII (56.39, 55.26, 40.2); $[Hg(THEC)]^{2+}$ (0.020 mol dm^{-3}), ABI (56.05, 55.64, 39.0), ABII (55.63, 54.57, 39.2); $[Cd(THEC)]^{2+}$ (0.020 mol dm^{-3})[1], ABI (55.36, 56.13, 39.0), ABII (54.54, 53.81, 39.3).

carbon ^{13}C resonances of $[M(THEC)]^{2+}$ are given in Table I, but as a consequence of the poor signal to noise ratio, the errors in these parameters are large.

The mechanism shown in Figure 4 contrasts with that postulated for the intramolecular exchange of TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) (see structure) carbons in five-coordinate $[M(TMC)X]^+$ (M = Zn, Cd, Hg; X^- = monodentate anion), which proceeds through a Berry-type mechanism involving rearrangements between equivalent trigonal-bipyramidal structures in which TMC is in a folded trans I configuration and X^- occupies an axial site.[18,19] It also contrasts with the intramolecular exchange of cyclam (1,4,8,11-tetraazacyclotetradecane) carbons in five-coordinate $[Pb(cyclam)X]^+$ (X^- = monodentate anion), where cyclam interconverts between folded trans V R,R,R,R and S,S,S,S configurations.[20] These folded configurations require the two 1,3-diaminopropane medial carbons to be equivalent, consistent with the signal medial carbon resonance observed in the slow-exchange ^{13}C spectra of these complexes and in contrast to the two medial carbon resonances observed in the slow-exchange spectra of $[M(THEC)]^{2+}$. This clearly demonstrates the effect of displacing the noncoordinating proton and methyl moieties of cyclam and TMC with coordinating hydroxyethyl moieties of THEC on both complex structure and mechanism.

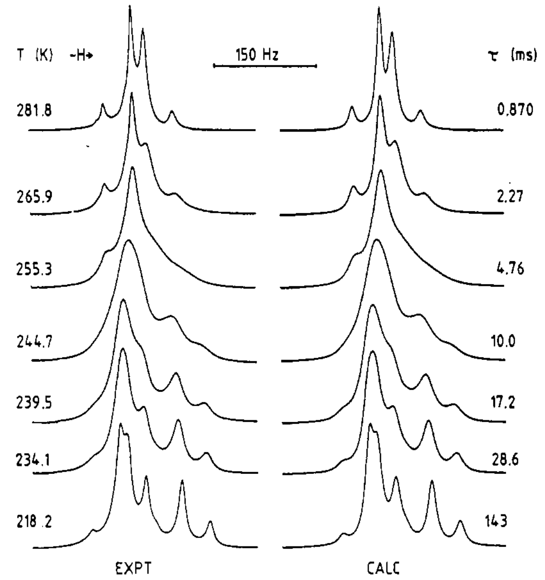

Figure 6. Temperature variation of ^{13}C 75.47-MHz NMR spectra of the 99% ^{13}C-enriched hydroxyethyl arms of $[Hg(THEC)]^{2+}$ (0.020 mol dm^{-3}) in CD_3OD. The experimental spectra and temperatures are on the left side, and the best fit calculated line shapes and the corresponding site lifetimes are on the right side.

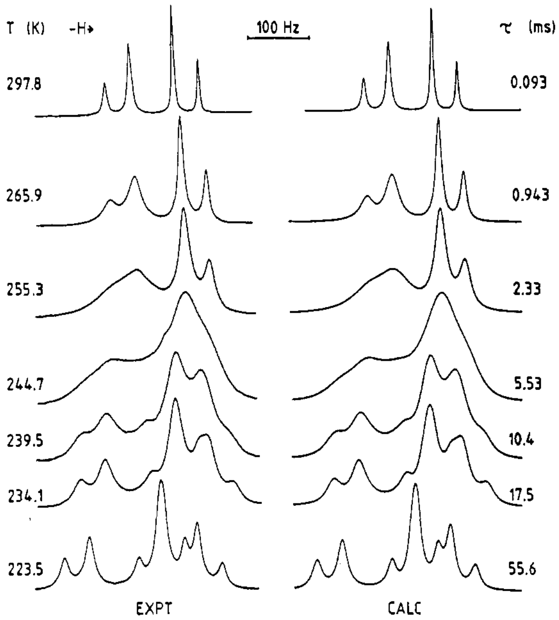

Figure 7. Temperature variation of ^{13}C 75.47-MHz NMR spectra of the 99% ^{13}C-enriched hydroxyethyl arms of $[Pb(THEC)]^{2+}$ (0.013 mol dm^{-3}) in CD_3OD. The experimental spectra and temperatures are on the left side, and the best fit calculated line shapes and the corresponding site lifetimes are on the right side.

^{13}C-Enriched $[M(THEC)]^{2+}$ Spectra and Intramolecular Exchange Processes. Under slow-exchange conditions the bidentate and monodentate hydroxyethyl arms (in which both methylene carbons of each of the hydroxyethyl arms are enriched to 99 atom % in ^{13}C) of $[M(THEC)]^{2+}$ are each characterized by ^{13}C AB quartets (Figure 5). It has been shown that the relative chemical shifts of the methylene carbons of the downfield quartet of $[Cd(THEC)]^{2+}$ are reversed by comparison to those of the upfield quartet.[1] Such a reversal of chemical shift does not occur for the Hg(II) and Pb(II) analogues, but the chemical shifts of their downfield quartets are substantially different. This is consistent

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(19) Alcock, N. W.; Curson, E. H.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1987–1993.

(20) Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1486–1491.

with the expectation that the bidentate hydroxyethyl arm should reflect the influence of variation in the nature of the metal center to a greater extent than the monodentate arm, and also that the bidentate arm should experience a greater electron withdrawal, and therefore be more deshielded than the monodentate arm. On this basis the downfield quartet is assigned to the bidentate arm.

The $[M(THEC)]^{2+}$ quartets coalesce to a single environmentally averaged quartet as the temperature is increased (Figures 6 and 7), and complete line-shape analysis using density matrix methods yields the kinetic parameters for the pairwise exchange of the hydroxyethyl arms given in Table I. (By contrast, and because of the reversal of the relative chemical shifts alluded to above, the quartets characterizing the mono- and bidentate arms of $[Cd(THEC)]^{2+}$ coalesce to a singlet under fast-exchange conditions.[1]) Despite the large error associated with the kinetic parameters derived from the natural abundance ^{13}C spectra, they are sufficiently similar to the parameters derived from the enriched ^{13}C spectra (Table I) to demonstrate that both coalescence phenomena arise from the same molecular process.

The proposed mechanism (Figure 4) is a highly concerted process in which no change in coordination number occurs. This is consistent with the moderate ΔH^{*} values observed (Table I), which are similar to those observed for related intramolecular processes for Cd(II)[19] and Pb(II)[20] TMC complexes. The variation of the metal ion in $[M(THEC)]^{2+}$ results in a decrease in rate for intramolecular exchange as the ionic radius increases from Cd(II) (95 pm) to Hg(II) (102 pm)[17] as a consequence of a substantially more negative ΔS^{*} characterizing $[Hg(THEC)]^{2+}$ (Table I). This is consistent with the larger Hg(II) more tightly fitting the macrocyclic hole of THEC than is the case for Cd(II) and thereby introducing a greater rigidity into the transition state envisaged in Figure 4. (The macrocyclic hole radius is estimated to be 135 pm on the basis of metal–nitrogen bond distances in similar systems.[21]) However, the group 14 cation, Pb(II), does not follow this trend in a uniform manner and kinetically is interposed between the two group 12 cations, Cd(II) and Hg(II). This may reflect a superimposition of the effect of difference in electronic structure between the two groups on the effect of cation size. Pb(II) has two more electrons than Hg(II), and evidence has been presented that these extra electrons can occupy a coordination site as a "stereochemically active" lone pair in macrocyclic ligand complexes where the ligand has three or more nitrogen donor atoms, with the effect that the coordination chemistry of Pb(II) resembles that of a smaller metal ion.[22,23] Thus, the lower stability of $[Pb(THEC)]^{2+}$ in water as seen in the variation of log $(K/\mathrm{dm^3\ mol^{-1}})$ = 9.38, 17.94, and 6.28 for $[M(THEC)]^{2+}$, where M = Cd, Hg, and Pb, respectively, may arise in part from the effect of the Pb(II) lone pair.[2] It is also possible that the greater lability of $[Pb(THEC)]^{2+}$ over $[Hg(THEC)]^{2+}$ in the intramolecular exchange observed in this study may be attributable to the effect of the Pb(II) lone pair, but it is inappropriate to speculate further on the basis of our limited range of kinetic data. We have also observed differences in solid-state characteristics between $[Pb(THEC)]^{2+}$ and its Cd(II) and Hg(II) analogues, as is shown below.

Solid-State Natural Abundance ^{13}C NMR Spectra. The solid-state CPMAS ^{13}C NMR spectra of $[M(THEC)]^{2+}$ are shown in Figure 8. When M = Cd and Hg, the spectra are characterized by two resonances at high field, attributable to inequivalent 1,3-diaminopropane moiety medial carbons, and a group of at least six resonances at lower field. These spectra bear a substantial resemblance to the slow-exchange solution spectra of $[Cd(THEC)]^{2+}$ and $[Hg(THEC)]^{2+}$, which suggests that the structures of $[Cd(THEC)]^{2+}$ and $[Hg(THEC)]^{2+}$ in the solid state and solution are similar. However, in the case of $[Pb(THEC)]^{2+}$ only a single resonance at high field is attributable to the medial carbons of the 1,3-diaminopropane moiety in contrast to the solution spectrum, where two well-resolved resonances are observed. This suggests that there is either a fortuitious magnetic equivalence of chemically inequivalent medial carbons in $[Pb(THEC)]^{2+}$ in the solid state or that the solid-state structure is different from the solution structure. The trans V configuration of the 1,4,8,11-tetraazacyclotetradecane has been observed in the solid state in *cis*-$[Ni(cyclam)(H_2O)_2]^{2+}$[24] and $[Pb(cyclam)(NO_3)_2]^{2+}$,[20] but in both cases the tetraaza ring is folded about a diagonal axis delineated by two nitrogens. If this folded trans V configuration was adopted by $[Pb(THEC)]^{2+}$ in the solid state, the four nitrogen atoms would occupy two cis and two trans sites in the coordination octahedron and the two remaining cis coordination sites would be occupied by the oxygens of the hydroxyethyl arms attached to the trans-coordinated nitrogens. (The hydroxyethyl arms attached to the cis-coordinated nitrogens could not coordinate in this configuration.) This structure possesses a C_2 axis, passing through Pb(II) and bisecting the angle made by the pair of cis-coordinated nitrogens and the angle made by the pair of cis-coordinated oxygens, which renders the medial carbons of the 1,3-diaminopropane moieties equivalent and compatible with the single resonance observed for these carbons in the solid-state spectrum. Eight further equivalent carbon pairs exist in this structure, and a total of nine resonances should be observed. Eight resonances are clearly resolved (Figure 8), and it is possible that some resonance superimposition obscures a ninth resonance in the region 50–60 ppm. Thus, a six-coordinate structure with THEC adopting a folded trans V configuration appears a plausible possibility for $[Pb(THEC)]^{2+}$ in the solid state.

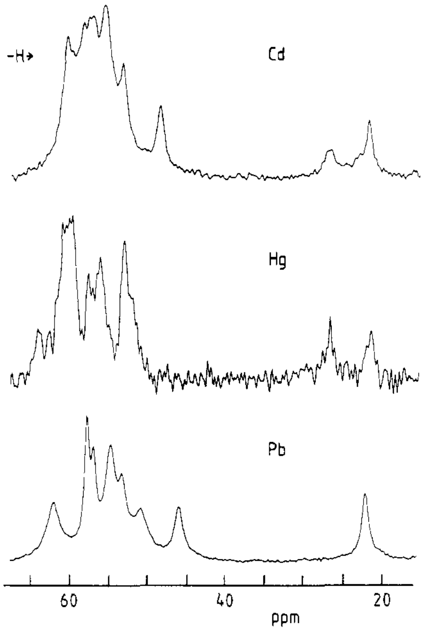

Figure 8. CPMAS ^{13}C 75.47-MHz NMR spectra of $[M(THEC)]^{2+}$. The frequencies are referenced to external adamantane. The two resonances at high field are assigned to the inequivalent medial carbons of the 1,3-diaminopropane moieties when M = Cd[1] and Hg. When M = Pb, the single high-field resonance is assigned to two magnetically equivalent medial carbons of the 1,3-diaminopropane moieties.

There is a tendency for Pb(II) to become eight-coordinate in the solid state, as exemplified by $[Pb(cyclam)(NO_3)_2]^{2+}$,[20] in which both nitrates act as bidentate ligands (and which has a structure similar to that suggested for six-coordinated $[Pb(THEC)]^{2+}$ in the solid state, where the two monodentate hydroxyethyl arms are each replaced by a bidentate nitrate). A structure similar to that observed for [1,4,7,10-tetrakis(2-hydroxypropyl)-1,4,7,10-tetraazacyclododecane]lead(II),[22] in which Pb(II) is coordinated by four nitrogens and four oxygens in a square-pseudoantiprismatic structure (with the ligand in a trans I configuration), would result

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in only seven resonances for $[Pb(THEC)]^{2+}$. Unfortunately, crystals suitable for X-ray diffraction determination of the crystal structures of $[M(THEC)](ClO_4)_2$ have not been obtained.

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Registry No. $[Hg(THEC)]^{2+}$, 130063-16-0; $[Pb(THEC)]^{2+}$, 130063-17-1; ^{13}C, 14762-74-4.

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Volumes of Activation for Electron Transfer between a Series of Cobalt Clathrochelates and Ferrocenes as a Function of Solvent and Added Electrolyte

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Electron-transfer rate constants for the reaction between a series of $Co(dioxime)_3(BX)_2$ compounds and either ferrocene or 1,1′-dimethylferrocene have been measured as a function of pressure, electrolyte, and solvent. Eight reactions were studied in acetonitrile as a function of pressure. Volumes of activation for these reactions ranged from -4 cm^3/mol for the reaction between $Co(dmg)_3(BC_6H_5)_2^+$ (dmg is doubly deprotonated dimethylglyoxime) and $Fe(CpCH_3)_2$ (Cp is cyclopentadienide), to -14 cm^3/mol for the reaction between $Co(dpg)_3(BC_6H_5)_2^+$ (dpg is doubly deprotonated diphenylglyoxime) and $Fe(CpCH_3)_2$. Volumes of activation generally became more negative with increasing size of the reactants. The reaction between $Co(dmg)_3(BF)_2^+$ and $FeCp_2$ was studied in both the forward and reverse directions. From these reactions, a volume of reaction of $+4$ cm^3/mol has been determined for the forward reaction. From the pressure derivative of the Marcus theory cross-reaction relation, a volume of activation for the electron self-exchange of $Co(dmg)_3(BF)_2^{0/+}$ has been calculated to be $\Delta V^* = -15$ cm^3/mol. The dependence of the volume of activation on added electrolyte was determined for the reactions of $Co(nox)_3(BF)_2^+$ (nox is doubly deprotonated cyclohexanedione dioxime) and $Co(dmg)_3(BF)_2^+$ with $FeCp_2$. For both reactions the volumes of activation become more negative with the addition of the salt tetrabutylammonium tetrafluoroborate. This is taken as further evidence for two paths of electron transfer, one being the reaction of the free ion and the other of the ion pair. The reactions between $Co(dmg)_3(BC_6H_5)_2^+$ with $Fe(CpCH_3)_2$ (reaction VI) and $Co(dmg)_3(BF)_2^+$ with $FeCp_2$ (reaction II) were studied as a function of solvent. The four solvents used were acetonitrile, methylene chloride, acetone, and nitrobenzene. Volumes of activation ranged from -4 to -14 cm^3/mol for reaction II and from -8 to -15 cm^3/mol for reaction VI. Trends in the data are discussed within current theories for the volume of activation.

Introduction

The measurement of volumes of activation has been shown to be an important tool for the elucidation of reaction mechanisms.[1-5] Recently there has been an increased use of this technique for the study of electron-transfer reactions.[6] Within transition-state theory, the volume of activation is defined as the difference between the volume of the transition state and that of the reactants and includes contributions from solvation of the reactants and the transition state. It is determined from the pressure dependence of the rate constant.[7] For outer-sphere electron-transfer processes, such as the reactions studied here, large, negative volumes of activation are often observed.[1,5,6]

Volumes of activation studies are increasing, but the majority of the work on electron-transfer reactions has been performed on reactions in aqueous media and on self-exchange systems where the only difference in the two reacting species is the oxidation state.[4] Our laboratory is especially interested in studying the effects of structure, solvent, and added electrolyte on volumes of activation.

The most commonly tested theory for the prediction of electron-transfer rate constants and how the rates vary with the parameters mentioned above is that of Marcus, especially as presented by Sutin.[8] A generalized example of the outer-sphere electron-transfer reaction is described as follows:

$$Co(dioxime)_3(BX)_2^+ + FeCp_2 \xrightleftharpoons{K_{OS}} Co(dioxime)_3(BX)_2^+{,}FeCp_2 \quad (1)$$

$$Co(dioxime)_3(BX)_2^+{,}FeCp_2 \xrightarrow{k_{et}} Co(dioxime)_3(BX)_2{,}FeCp_2^+ \quad (2)$$

$$Co(dioxime)_3(BX)_2{,}FeCp_2^+ \rightarrow Co(dioxime)_3(BX)_2 + FeCp_2^+ \quad (3)$$

The first step is the formation of an encounter complex with a formation constant K_{OS}. The second step is electron transfer, which occurs with a rate constant k_{et}. The final step represents the formation of the products from the successor complex. The rate law for such a mechanism is

$$d[Co(dioxime)_3(BX)_2]/dt = k_{et}K_{OS}[Co(dioxime)_3(BX)_2^+][FeCp_2] \quad (4)$$

It is the product $k_{et}K_{OS}$ that is measured as a function of pressure and is defined as the observed second-order rate constant. Thus the volume effects associated with the formation of the encounter complex, as well as the actual electron-transfer process, contribute to the observed value of ΔV^*.

The work presented here is a continuation of our study of electron transfer on a series of cobalt clathrochelates.[9-13] The reactions studied are as follows:

$$Co(nox)_3(BF)_2^+ + FeCp_2 \rightleftharpoons Co(nox)_3(BF)_2 + FeCp_2^+ \quad (I)$$

$$Co(dmg)_3(BF)_2^+ + FeCp_2 \rightleftharpoons Co(dmg)_3(BF)_2 + FeCp_2^+ \quad (II)$$

$$Co(dpg)_3(BC_6H_5)_2^+ + FeCp_2 \rightleftharpoons Co(dpg)_3(BC_6H_5)_2 + FeCp_2^+ \quad (III)$$

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