Articles

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Carbon-13 and Cadmium-113 Nuclear Magnetic Resonance Evidence for a Novel Transannular Oscillation of Cadmium(II) in the Pendant Arm Macrocyclic Complex [1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane]cadmium(II)

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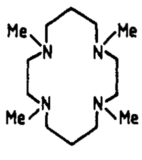
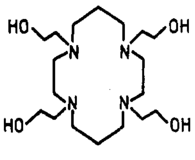
A ^{13}C NMR study of [1,4,8,11-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane]cadmium(II), $[Cd(THEC)]^{2+}$, in CD_3OD shows that the most probable structure for $[Cd(THEC)]^{2+}$ incorporates the 1,4,8,11-tetraazacyclotetradecane ring in the trans III configuration. In this structure Cd(II) is above the tetraaza plane and is trigonal-prismatically coordinated by four ring nitrogens and two hydroxyethyl pendant arms attached to either end of the same 1,3-diaminopropane moiety. The ^{13}C CPMAS NMR spectrum of solid $[Cd(THEC)]^{2+}$ is also consistent with this structure. Dynamic ^{13}C NMR studies of natural abundance $[Cd(THEC)]^{2+}$ and of $[Cd(THEC)]^{2+}$ in which both carbons of each of the hydroxyethyl arms are 99 atom % enriched in ^{13}C are consistent with a rapid oscillation of Cd(II) through the macrocyclic annulus of THEC. The ^{13}C-enriched hydroxyethyl arms are characterized by ^{13}C AB quartets under conditions of slow exchange but show a novel coalescence to a singlet under fast-exchange conditions consistent with the relative chemical shifts of the methylene carbons of the hydroxyethyl arm being reversed when it changes from the mono- to the bidentate coordination state. The pairwise exchange of the hydroxyethyl arm between the monodentate and bidentate environments is characterized by $k(298.2\ K) = 34200 \pm 1800\ s^{-1}$, $\Delta H^{*} = 44.00 \pm 0.56\ kJ\ mol^{-1}$, and $\Delta S^{*} = -10.6 \pm 2.2\ J\ K^{-1}\ mol^{-1}$. ^{13}C and ^{113}Cd NMR spectra show that intermolecular THEC and Cd(II) exchange on $[Cd(THEC)]^{2+}$ is a much slower process.

Complexation of metal ions by pendant donor arm polyazamacrocyclic ligands has attracted substantial attention in the search for metal ion selective ligands, and the resulting metal complexes exhibit a considerable variation in structure and lability that depends substantially on the nature of the pendant arm.[1-9] Thus, for ligands based on 1,4,8,11-tetraazacyclotetradecane (cyclam), where the pendant arms are in the 1-, 4-, 8-, and 11-positions, metal complexation takes several hours to reach equilibrium when the pendant arms lack donor groups, as in 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC), while equilibrium is reached in seconds when the pendant arms possess donor groups, as in 1,4,8,11-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane (THEC).[1,2] This increased rate of complexation is probably a consequence of fast initial coordination of the metal ion by the flexible hydroxyethyl arms. This generates a high local metal ion concentration in the vicinity of the less flexible tetraaza ring and greatly increases the rate of coordination of the metal ion by the tetraaza ring. This supposition is supported by the observation that the weakly coordinating 2-cyanoethyl pendant arm causes no significant rate increase.[1,5] When the donor strength is increased over that of 2-hydroxyethyl, as for pendant arms such as 2-aminoethyl,[6] 3-aminopropyl,[7] or 2-pyridylmethyl,[8] the metal ion may be coordinated by two pendant arm donor groups and only two of the nitrogens of the tetraaza ring in the final complex. Thus the metal ion remains outside the macrocyclic annulus and potential discrimination between metal ions due to the size compatibility of the annulus and the metal ion is lost. However, when acetate is the pendant arm, the metal is coordinated by the four nitrogens of the tetraaza ring and by two acetate pendant arms.[9]



TMC



THEC

The 2-hydroxyethyl arm may be an optimum type of donor pendant arm as it both accelerates metal complexation and retains the potential size selectivity of the macrocyclic annulus as the metal ion is coordinated by all four nitrogens of the tetraaza ring, as observed in the solid state for $[Ni(THEC^{*})]^{+}$ ($THEC^{*}$ = deprotonated THEC).[2] No other solid-state structure is available for a THEC complex, and the solution structures of THEC complexes are not known with any certainty. As part of a study of the complexation of heavy-metal ions by pendant arm polyazamacrocyclic ligands, we selected $[Cd(THEC)]^{2+}$ for study, as it is diamagnetic and therefore its natural abundance and selectively enriched ^{13}C NMR spectra should yield both structural and kinetic information. In addition, the considerable sensitivity of the ^{113}Cd shift to environment[10] should be valuable in deducing the number of $[Cd(THEC)]^{2+}$ complexes formed.

Experimental Section

Synthesis of [1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane]cadmium(II) Perchlorate ($[Cd(THEC)](ClO_4)_2$).

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1,4,8,11-Tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane (THEC) was prepared and purified according to literature methods.[1] The ^{13}C enrichment of all 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. $[Cd(THEC)](ClO_4)_2$ was prepared in the following way. A solution of hexaaquacadmium(II) perchlorate (0.64 g, 1.5 mmol) in 1-butanol (20 cm^3) was added dropwise to a stirred, refluxing solution of THEC (0.58 g, 1.5 mmol) in 1-butanol (20 cm^3). The resulting suspension was stirred and refluxed for a further 20 min before allowing it to cool slowly to room temperature. The mixture was chilled overnight at 278 K and then filtered under a positive pressure of argon. The white microcrystalline precipitate was washed with diethyl ether (3 × 10 cm^3) and then dried in vacuo to give the pure product (0.96 g, 93%). Anal. Calcd for $C_{18}H_{40}CdCl_2N_4O_{12}$: C, 31.4; H, 5.9; N, 8.2. Found: C, 31.5; H, 5.9; N, 8.0. IR (Nujol): 3425 cm^{-1} br (ν_{O-H}). Λ_M: 157 $cm^2\ \Omega^{-1}\ mol^{-1}$ (MeOH) (1:2).[11]

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) and ^{113}Cd (66.55 MHz) spectra were run on a Bruker CXP-300 spectrometer locked on deuterium. Solution samples were prepared under an atmosphere of argon by using CD_3OD that had been dried over Linde 3-Å molecular sieves. The ^{13}C solution spectra were run with broad-band proton decoupling, and for each solution an average of 6000 transients was accumulated in a 2048 point data base at temperature intervals of ca. 5 K. 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.[12,13] The Fourier transformed spectra were subjected to complete line-shape analysis on a VAX 11780 computer using a density matrix method similar to that described elsewhere.[14-16] 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 chemical 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.[17]

The CPMAS ^{13}C spectra of solid-state samples were recorded by using standard methods. Chemical shifts were referenced to the lowfield resonance of external adamantane, which was assigned a chemical shift of 38.23 ppm.

The ^{113}Cd spectra were run without decoupling, and chemical shifts were referenced to external 0.10 mol dm^{-3} $Cd(ClO_4)_2$ in D_2O assigned a chemical shift of 0.00 ppm.[18] It was found that the ^{113}Cd spectra were incompletely relaxed for recycle delays of less than 5 s, and accordingly, spectra were run with a delay of 10 s.

Results and Discussion

Natural Abundance ^{13}C and ^{113}Cd NMR Solution Spectra. At 293.0 K the natural abundance ^{13}C spectra of free THEC and $[Cd(THEC)]^{2+}$ (both 0.050 mol dm^{-3} in CD_3OD solution) each exhibit five resonances in the approximate intensity ratio 2:2:2:2:1 at 58.55, 54.57, 51.13, 49.30, and 23.69 ppm and 58.42, 55.50, 55.41, 51.59, and 22.58 ppm, respectively, in CD_3OD. In the THEC spectrum the resonances at 58.55 and 54.57 ppm are assigned to the hydroxyethyl arm carbons (by comparison with the ^{13}C-enriched spectrum) and the resonance at 23.69 ppm is assigned to the medial carbon of the 1,3-diaminopropane moiety. In the $[Cd(THEC)]^{2+}$ spectrum the resonances at 55.50 and 55.41 ppm are assigned to the hydroxyethyl arm carbons (by comparison with the ^{13}C-enriched spectrum) and the resonance at 22.58 ppm is assigned to the medial carbon of the 1,3-diaminopropane moiety. In both spectra the remaining two resonances arise from the 1,2-diaminoethane moiety and the $-NCH_2$ of the 1,3-diaminopropane moiety.

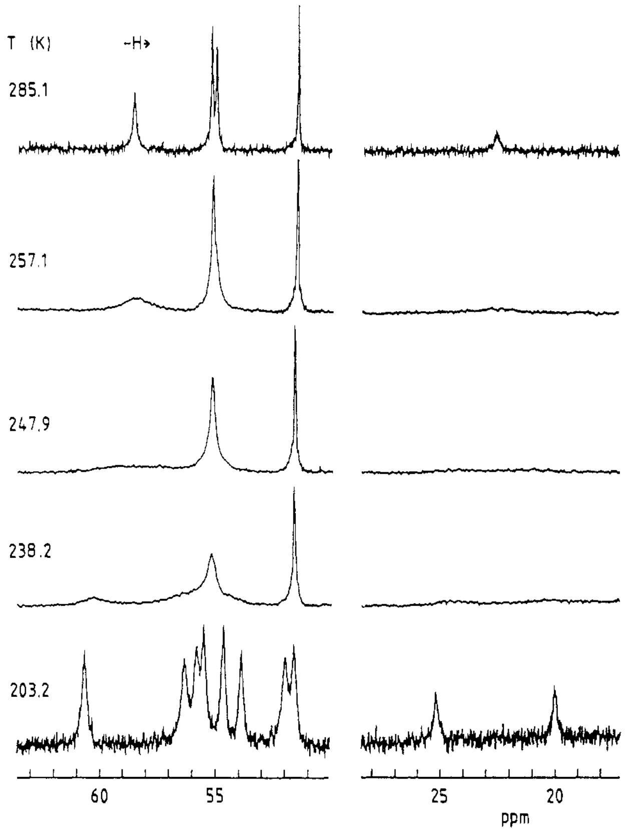

Figure 1. Temperature variation of the ^{13}C 75.47-MHz broad-band proton-decoupled NMR spectrum of $[Cd(THEC)]^{2+}$ (0.050 mol dm^{-3}) in CD_3OD.

The observation of separate ^{13}C NMR spectra for THEC and $[Cd(THEC)]^{2+}$ indicates that intermolecular ligand exchange is in the slow-exchange regime of the NMR time scale, and an upper limit for the intermolecular THEC exchange rate constant, k_{THEC}, may be obtained through

$$1.5\pi W_{1/2\,obs} - \pi W_{1/2\,obs} = 1/\tau_{THEC} = k_{THEC} \qquad (1)$$

where $W_{1/2\,obs}$ is the observed width (Hz) of the $[Cd(THEC)]^{2+}$ resonance at half amplitude, $1.5W_{1/2\,obs}$ is the width that would be observed if the rate of intermolecular ligand exchange is arbitrarily chosen to be sufficient to increase the natural line width by half, and τ_{THEC} is the mean lifetime of THEC in $[Cd(THEC)]^{2+}$. The $W_{1/2\,obs}$ values range from 5.0 to 8.8 Hz, and the upper limit of $k_{THEC}(293.0\ K) = 8-14\ s^{-1}$, calculated through eq 1. (The medial carbon resonance exhibits broadening from the intramolecular exchange process discussed below and was not used in the calculation of k_{THEC}.)

The free THEC spectrum retains its five resonances as temperature is decreased, while each of the $[Cd(THEC)]^{2+}$ resonances splits into two equal intensity resonances at low temperature, as seen in Figure 1. This reversible coalescence phenomenon is consistent with each carbon exchanging between two inequivalent sites and simultaneous exchange of Cd(II) between two sites in $[Cd(THEC)]^{2+}$. The $[Cd(THEC)]^{2+}$ pattern of five symmetrical pairs of resonances requires the two 1,3-diaminopropane moieties to be inequivalent with the two inequivalent medial carbons being either within the same plane of symmetry or on a C_2 axis characterizing the $[Cd(THEC)]^{2+}$ structure. In principle Cd(II) could be coordinated by two nitrogens at either end of the 1,3-diaminopropane moiety and the two hydroxyethyl arms of that moiety. Exchange of Cd(II) between this site and the equivalent site based on the second 1,3-diaminopropane moiety could account for the coalescence seen in Figure 1 but in addition should also facilitate intermolecular Cd(II) exchange.

^{113}Cd NMR spectroscopy shows a single resonance for $[Cd(THEC)]^{2+}$ ($W_{1/2}$ = 70 Hz), indicating the presence of only one complex, and a narrower resonance for solvated Cd(II) ($W_{1/2}$ =

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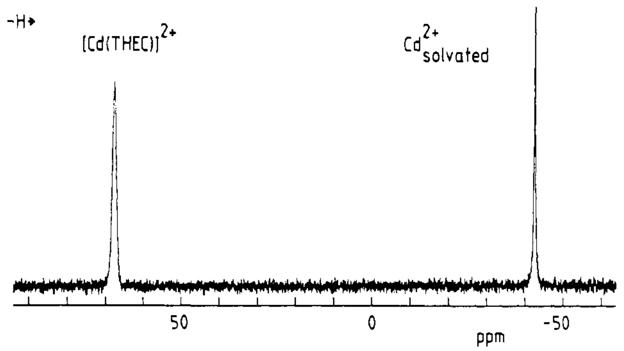

Figure 2. ^{113}Cd 66.55-MHz NMR spectrum of a solution of $[Cd(THEC)](ClO_4)_2$ (0.100 mol dm^{-3}) and $Cd(ClO_4)_2$ (0.067 mol dm^{-3}) at 300.6 K (4900 transients, recycle delay 10 s). The frequencies are referenced to external 0.10 mol dm^{-3} $Cd(ClO_4)_2$ in D_2O.

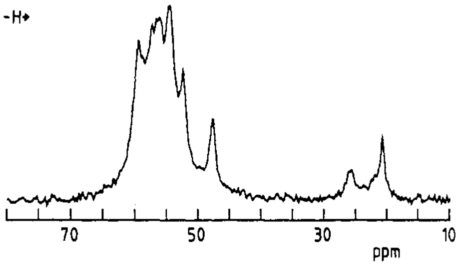

Figure 3. CPMAS ^{13}C 75.47-MHz NMR spectrum of $[Cd(THEC)]^{2+}$. The frequencies are referenced to the low-field resonance of external adamantane assigned a shift of 38.23 ppm. The two resonances at high field are assigned to the inequivalent medial carbons of the 1,3-diaminopropane moiety.

28 Hz) at 300.6 K, as seen in Figure 2. (The 0.10 mol dm^{-3} $Cd(ClO_4)_2$ in D_2O reference solution $W_{1/2} = 3$ Hz.) The downfield shift of $[Cd(THEC)]^{2+}$ from $[Cd(CD_3OD)_6]^{2+}$ (the assumed stoichiometry of solvated Cd(II)) is consistent with the ^{113}Cd deshielding usually observed as oxygen donor atoms are displaced by nitrogen donor atoms in the first coordination sphere.[19,20] The large $W_{1/2}$ of $[Cd(THEC)]^{2+}$ probably arises from a combination of unresolved coupling with ^1H and ^{14}N and chemical shift anisotropy relaxation.[10,19,21] A probable cause of the large $W_{1/2}$ of $[Cd(CD_3OD)_6]^{2+}$ is deuterium coupling with $-CD_3$. Both resonances narrow slightly at higher temperatures and broaden at lower temperatures, consistent with intermolecular exchange between $[Cd(THEC)]^{2+}$ and solvated Cd(II) being at the extreme slow-exchange limit at 300.6 K. An upper limit for the rate constant for intermolecular Cd(II) exchange between $[Cd(THEC)]^{2+}$ and free Cd(II), $k_{Cd(II)} = 110\ s^{-1}$, may be calculated from $W_{1/2\,obs} = 70$ Hz for $[Cd(THEC)]^{2+}$ at 300.6 K through an expression similar to eq 1. The k_{THEC} and $k_{Cd(II)}$ values are much less than $k(298.2\ K) = 68000 \pm 18000\ s^{-1}$ for the medial carbon exchange process derived from complete line-shape analysis of the coalescence of the ^{13}C medial carbon spectra and thereby eliminate intermolecular exchange of Cd(II) or THEC as a significant pathway for medial carbon exchange. (The large error in k is due to the poor signal to noise ratio of the natural abundance ^{13}C spectra. A more accurate determination of $k(298.2\ K) = 34200 \pm 1800\ s^{-1}$ is obtained through 99% atom enriched ^{13}C $[Cd(THEC)]^{2+}$ as discussed below.)

Solution Structure of $[Cd(THEC)]^{2+}$. A knowledge of the structure of $[Cd(THEC)]^{2+}$ is essential to the interpretation of its ^{13}C NMR spectral coalescence. Unfortunately, crystals suitable for an X-ray diffraction determination of the solid-state structure of $[Cd(THEC)](ClO_4)_2$ have not been obtained. However, the solid-state CPMAS ^{13}C NMR spectrum (Figure 3) is 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 and generally bears a marked resemblance to the slow-exchange solution spectrum of $[Cd(THEC)]^{2+}$. This suggests that the structures of $[Cd(THEC)]^{2+}$ in the solid state and solution are similar.

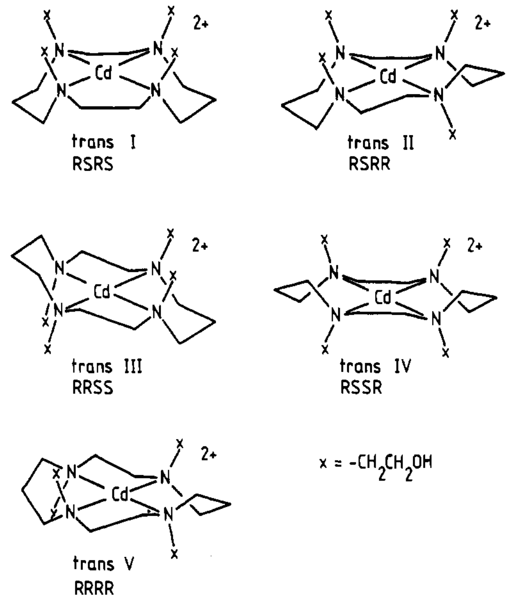

Figure 4. Possible configurational isomers of $[Cd(THEC)]^{2+}$ in which the hydroxyethyl arms are shown uncoordinated.

The basis for the deduction of the $[Cd(THEC)]^{2+}$ structure from the slow-exchange ^{13}C NMR solution spectrum (Figure 1) is that the pattern of five symmetrical pairs of resonances requires the medial carbons of the two 1,3-diaminopropane moieties to be inequivalent but either within the same plane of symmetry or on a C_2 axis characterizing the $[Cd(THEC)]^{2+}$ structure. Such structures require Cd(II) to be coordinated by the four nitrogens of the tetraaza ring and the two hydroxyethyl arms at either end of the same 1,3-diaminopropane moiety. The five configurations possible for the THEC 1,4,8,11-tetraazacyclotetradecane ring with a planar array of nitrogens coordinating Cd(II) are shown in Figure 4, but no indication of the pairwise coordination of the hydroxyethyl arms is shown.

The trans II configuration does not provide the basis for a possible structure as, irrespective of the pairwise coordination of the hydroxyethyl arms, it would produce asymmetric $[Cd(THEC)]^{2+}$ structures characterized by separate ^{13}C resonances for each of the 18 inequivalent carbons. Examination of the four remaining configurations shows that each could produce five pairs of ^{13}C resonances for $[Cd(THEC)]^{2+}$ and retain the inequivalence of the medial carbons of the 1,3-diaminopropane moiety only if pairwise coordination of the hydroxyethyl arms at either end of the same 1,3-propanediamine moiety occurs. (Any other pairwise coordination of the hydroxyethyl arms renders the medial carbons equivalent.) Under these constraints trans coordination of the hydroxyethyl arms to Cd(II) is required by the trans IV and trans V THEC configurations, which both incorporate the skew-boat conformation for the six-membered chelate rings formed by coordination of the 1,3-propanediamine moiety to Cd(II). It is probably a consequence of the thermodynamically unstable nature of the skew-boat configuration that no complexes involving ligands incorporating the 1,4,8,11-tetraazacyclotetradecane ring have been observed in the trans IV configuration, and on this basis this configuration is considered unlikely for $[Cd(THEC)]^{2+}$.

Complexes have been observed incorporating the 1,4,8,11-tetraazacyclotetradecane ring in the trans V configuration but only after folding of this ring about a diagonal axis delineated by two nitrogens such that these nitrogens occupy the trans coordination sites of an octahedral metal ion, the other two nitrogens occupy cis Cd(II) coordination sites, and the remaining two cis coordination sites are occupied by other donor groups (as exemplified by *cis*-$[Ni(cyclam)(H_2O)_2]^{2+}$).[22] If this folded trans V

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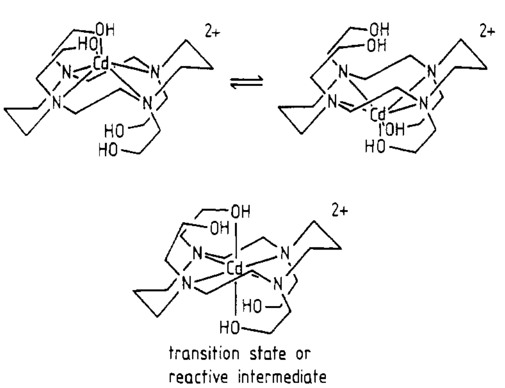

Figure 5. Proposed [Cd(THEC)]$^{2+}$ structure and transannular exchange mechanism.

configuration was adopted by [Cd(THEC)]$^{2+}$, the hydroxyethyl arms attached to the trans coordinated nitrogens would coordinate in the remaining two cis coordination sites (while the hydroxyethyl arms attached to the cis coordinated nitrogens would not coordinate). This structure possesses a C_2 axis (passing through Cd(II) and bisecting the angle made by the pair of cis coordinated nitrogens and the angle made by the pair of cis coordinated hydroxyethyl arms), which renders the medial carbons of the 1,3-diaminopropane moieties equivalent, and is thus incompatible with the inequivalence of these carbons observed in the slow-exchange ^{13}C NMR spectrum.

The trans I configuration readily provides for the pairwise coordination of hydroxyethyl arms attached to the same 1,3-diaminopropane moiety. However, this configuration should also provide for the coordination of hydroxyethyl arms attached to diagonally related nitrogens, or two nitrogens of the same 1,2-diaminoethane moiety, both of which structures would produce equivalence of the medial carbons of the 1,3-diaminopropane moieties. No resonances attributable to the latter two structural possibilities are detectable in the slow-exchange ^{13}C NMR spectrum. Accordingly, the trans I configuration is discounted as a possibility for [Cd(THEC)]$^{2+}$ even though it is the binding configuration commonly adopted by ligands of this type with weak or noncoordinating pendant arms.[4,23,24]

The most plausible explanation of the medial carbon inequivalence is presented by a structure incorporating the trans III configuration, in which Cd(II) lies above the tetraaza plane and is trigonal-prismatically coordinated by two hydroxyethyl arms and the four ring nitrogens, as shown in the equivalent structures in Figure 5. (Trigonal-prismatic coordination of Cd(II) has been reported in the solid state for K[Cd(acac)$_3$][25] and more recently in a polyazamacrocyclic complex.[26])

The simplest mechanism for exchange of the medial carbons and the pairwise exchange of the other carbons appears to be the transannular oscillation of Cd(II) shown in Figure 5. The transition state or reactive intermediate for this mechanism is envisaged to have Cd(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. Support for this mechanism is afforded by the crystal structure of the Ni(II) complex of deprotonated THEC, in which THEC is in the trans III configuration and Ni(II) is 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 for the proposed [Cd(THEC)]$^{2+}$ transition state (Figure 5).[27]

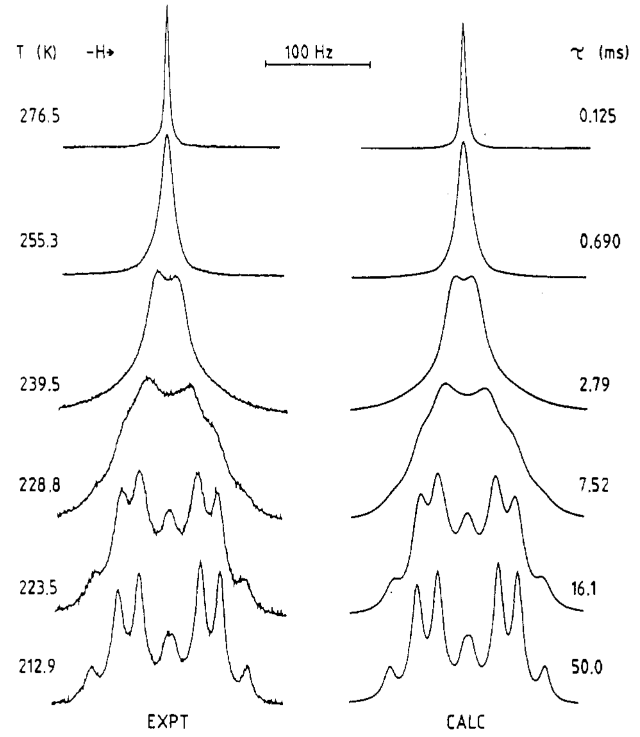

Figure 6. Temperature variation of the ^{13}C 75.47-MHz NMR spectrum of the 99% ^{13}C-enriched hydroxyethyl arms of [Cd(THEC)]$^{2+}$ (0.020 mol dm^{-3}) in CD$_3$OD. For the downfield and upfield quartets $J(^{13}C-^{13}C)$ = 39.0 and 39.3 Hz, respectively. The experimental spectra and temperatures are at the left-hand side and the best-fit-calculated line shapes and the corresponding site lifetimes are at the right-hand side.

The mechanism shown in Figure 5 contrasts with that postulated for the intramolecular exchange of TMC carbons in five-coordinate [Cd(TMC)X]$^+$ (X$^-$ = monodentate anion), which proceeds through a Berry-type mechanism involving rearrangements between equivalent trigonal-bipyramidal structures in which TMC is in a folded configuration and X$^-$ occupies an axial site.[29] This mechanism requires the two 1,3-diaminopropane medial carbons to be equivalent, consistent with the single medial carbon resonance observed in the slow-exchange ^{13}C NMR spectrum of [Cd(TMC)X]$^+$ and in contrast to the two ^{13}C resonances observed for the inequivalent medial carbons of [Cd(THEC)]$^{2+}$. This clearly demonstrates the effect of replacing the noncoordinating methyl moieties of TMC with the coordinating hydroxyethyl moieties of THEC on both complex structure and reaction mechanism.

^{13}C-Enriched [Cd(THEC)]$^{2+}$ Spectra and Intramolecular Exchange Processes. To better determine the kinetic parameters of this exchange process, both methylene carbons of each of the hydroxyethyl arms were enriched to 99 atom % in ^{13}C. As a consequence, both the bidentate and monodentate hydroxyethyl arms are characterized by ^{13}C AB quartets (where the downfield quartet is tentatively assigned to the bidentate hydroxyethyl arm on the basis that it is likely to experience the greater decrease of electron density through bidentate coordination) under slow-exchange conditions, as seen in Figure 6. However, under fast-exchange conditions these quartets coalesce to a singlet consistent with the relative chemical shifts of the N–CH$_2$ and HO–CH$_2$

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(27) An explanation for the difference between the structure determined from X-ray crystallography for the Ni(II) complex of deprotonated THEC and that deduced from ^{13}C NMR data for [Cd(THEC)]$^{2+}$ is that the ionic radius[28] of Cd(II) (97 pm) is greater than that of Ni(II) (69 pm) such that the latter metal ion is more readily accommodated by the macrocyclic annulus of THEC.

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carbons being reversed on coordination of the hydroxyethyl arm hydroxyl group. Complete line-shape analysis of the reversible coalescence of the two AB quartets (using a density matrix program based on methods similar to those described elsewhere) yields the best-fit line shapes shown in Figure 6, and $k(250.0\ \text{K}) = 940 \pm 20\ \text{s}^{-1}$, $k(298.2\ \text{K}) = 34200 \pm 1800\ \text{s}^{-1}$, $\Delta H^{*} = 44.00 \pm 0.56$ kJ mol^{-1}, and $\Delta S^{*} = -10.6 \pm 2.2$ J K^{-1} mol^{-1} for exchange of the hydroxyethyl arms, where the errors represent one standard deviation for the fit of the τ data to the Eyring equation. (The $k(250$ K) value is the more reliable as it is derived at the midpoint of the spectral coalescence temperature range.) These parameters compare with $k(250.0\ \text{K}) = 1530 \pm 200\ \text{s}^{-1}$, $k(298.2\ \text{K}) = 68000 \pm 18000\ \text{s}^{-1}$, $\Delta H^{*} = 46.6 \pm 4.5$ kJ mol^{-1}, and $\Delta S^{*} = 4 \pm 15$ J K^{-1} mol^{-1} for exchange of the medial carbons derived through complete line-shape analysis of the medial doublet coalescence seen in Figure 1. Due to a substantially poorer signal to noise ratio characterizing the natural-abundance ^{13}C spectra, the latter data set is subject to higher error, but they are in sufficient agreement with the data derived from the enriched ^{13}C spectra to demonstrate that both coalescence phenomena arise from the same molecular process.

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Chiroptical Properties of a Compound Containing a Metal–Metal Quadruple Bond. Synthesis, Structure, and Spectra of β-$Mo_2Cl_4(S,S\text{-bppm})_2$, Where *S*,*S*-bppm is (2*S*,4*S*)-*N*-(*tert*-Butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine

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The complex, β-Mo_2Cl_4(*S*,*S*-bppm)$_2$ is prepared by reaction of $K_4Mo_2Cl_8$ with (2*S*,4*S*)-*tert*-butyl 4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-1-pyrrolidinecarboxylate (*S*,*S*-bppm). Its UV–vis, CD, IR, and NMR spectra have been recorded, and its structure has been determined. Crystal data: space group $P2_12_12_1$, $a = 19.812$ (4) Å, $b = 20.609$ (2) Å, $c = 17.815$ (3) Å, V = 7273 (2) Å^3, $Z = 4$, with final residuals $R = 0.0698$ and $R_w = 0.0852$. This complex has a average twist angle of about 0°. The circular dichroism spectrum of this complex shows two prominent bands at 580 and 492 nm which can be assigned to $\delta_{xy} \rightarrow \delta^*_{xy}$ and $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transitions, respectively. The one-electron, static coupling mechanism is used to account for the observation of the circular dichroism bands.

Introduction

Dimetal complexes of the type β-$Mo_2X_4(PP)_2$, where PP is a diphosphine ligand, have been extensively studied during the last few years.[1,2] An interesting property of this type of complex is that the molecules adopt a staggered or partially staggered geometry around the metal–metal bond due to ligand constraints. Thus, complexes of this type are configurationally chiral,[3] but due to the rapid racemization in solution, these complexes are not optically active and no measureable CD spectrum under the $\delta \rightarrow \delta^*$ transition can be detected, even though the complexes sometimes crystallize as enantiomorphic single crystals. Introducing a chiral ligand of a type that causes the complex to twist preferentially in one direction has become a major method in studying the CD spectra of such complexes.[4] The conformational preference of the ligand effects an asymmetric synthesis and thereby produces only one of the configurational isomers, and this in turn enables the CD spectrum to be measured. Until now only three[4,5] complexes of this kind have been structurally characterized, all of which may be classified[6] as being "case I" chromophores. In this paper, we report the first compound that appears to belong to the "case II" class of chromophore.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry oxygen-free argon by using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. Methanol was purified by distillation from magnesium, *n*-hexane from sodium-potassium/benzophenone, and dichloromethane from P_2O_5. The visible absorption spectrum of Mo_2Cl_4(*S*,*S*-bppm)$_2$ in dichloromethane was recorded on a Beckman DU 70 spectrophotometer. The IR spectrum was recorded on an IBM FTIR/40S spectrometer by pressing the sample in KBr disks. The circular dichroism (CD) spectra were obtained on a Jacso J-600 spectrophotometer. The $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Varian XL-200 NMR spectrometer.

Starting Materials. $K_4Mo_2Cl_8$ was prepared according to a previously reported[7] procedure. The ligand (2*S*,4*S*)-*N*-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (*S*,*S*-bppm) was purchased from Aldrich Chemical Co..

Preparation. $K_4Mo_2Cl_8$ (0.1 g, 0.158 mmol) and *S*,*S*-bppm (0.18 g, 0.325 mmol), were placed in a flask equipped with a reflux condenser. Methanol (13 mL) was then added. This mixture was refluxed for 3 h to yield a blue solution and a blue solid. The solid was filtered off, washed with methanol and ether, and then dried under reduced pressure. Yield: 0.11 g (48%). IR (KBr disk): 1615 ($\nu_{C=O}$) cm^{-1}. Solutions of this complexes are slightly air-sensitive, but solid samples are air-stable.

Crystals suitable for X-ray diffraction measurement were obtained by hexane-induced crystallization from a dichloromethane solution.

X-ray Crystallography. The structure of β-Mo_2Cl_4(*S*,*S*-bppm)$_2$ was determined by general procedures that have been fully described elsewhere.[8] The diffraction data were collected on a Syntex P3 equivalent diffractometer at 20 ± 1 °C, which was equipped with graphite-monochromated Mo Kα ($\lambda_\alpha = 0.71037$ Å) radiation. Data reduction was carried out by standard methods with the use of well-established computational procedures.[9] Basic information pertaining to crystal parameters and structure refinement are summarized in Table I. Tables II and III list positional parameters and selected bond distances and angles, respectively.

A deep blue crystal of β-Mo_2Cl_4(*S*,*S*-bppm)$_2$ was mounted on the top of a glass fiber with epoxy cement. A rotational photograph indicated that the crystal diffracted well. The unit cell constants were determined

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