Natural Abundance ^{15}N Nuclear Magnetic Resonance Spectroscopy of Heavy Metal Complexes of *trans*-1,2-Diaminocyclohexane-*NNN'N'*-tetra-acetate Ion and 1,4,8,11-Tetra-azacyclotetradecane

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Natural abundance ^{15}N n.m.r. spectra of aqueous solutions of *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetate ion (cydta^{4-}) and its metal complexes have been observed for the metal ions Cd^{II}, Hg^{II}, Ag^{I}, and Pb^{II}, and ^{1}J metal–nitrogen spin couplings for $^{111}Cd^{II}$, $^{113}Cd^{II}$, $^{199}Hg^{II}$, and $^{207}Pb^{II}$ measured. These spin couplings are compared with those obtained for the same metal ions complexed with the macrocycle 1,4,8,11-tetra-azacyclotetradecane (L). The co-ordination shifts of the ligands are consistently small and to low field. The ^{15}N spectra of $[Cd(L)][NO_3]_2$ and $[Hg(L)][ClO_4]_2$ are reported, and the variable-temperature profile of the spectra for $[Cd(L)][NO_3]_2$ confirm earlier ^{13}C results which showed the complex to be a mixture of two isomers in solution. The two species have square and dynamically folded trigonal-bipyramidal nitrogen-donor sets with configurations *R,S,S,R* and *R,S,R,S* respectively. The different values of $^{1}J(M-^{15}N)$ for the two nitrogen sites in folded complexes of L with Cd^{II} and Pb^{II} are discussed in terms of rehybridisation of the Pb^{II} orbitals, and for Cd^{II} the percentage *s* character of the relevant hybrid orbitals.

THE application of ^{15}N n.m.r. spectroscopy for the study of complexes containing *N*-donor ligands has been severely limited because of the problems of low n.m.r. sensitivity (1.04×10^{-3} that of protons for equal numbers of nuclei) and low natural abundance (0.3%) associated with this nucleus. Further problems can arise from unfavourable spin–lattice relaxation times and the possibility of signal nulling as the nuclear Overhauser enhancement approaches a value of -1.[1] However, recent advances in instrument design, notably the use of high magnetic fields (4.08 T) and large sample volumes (*ca.* 15 cm^3) have greatly facilitated the observation of ^{15}N spectra at natural abundance. The availability of such new instrumentation together with the favourable solubility of our complexes has prompted us to explore the use of ^{15}N spectroscopy, at natural abundance, in our studies of complex formation between tetra-azamacrocyclic ligands (*e.g.* cyclam, L) and the heavy metal ions of cadmium, mercury, and lead. For the purpose of comparison, and to supplement the sparse literature data [2-5] on one-bond spin coupling between metal ions and ^{15}N, we have also studied a series of complexes of *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetate ion (cydta^{4-}) formed with cadmium, mercury, silver, and lead ions. The cydta^{4-} ion was chosen for study because previous work [6] has shown that its complexes are more stable and inert to ligand exchange than those of the closely related ligand, edta^{4-} (the ethylenediaminetetra-acetate ion).

EXPERIMENTAL

The complexes $[Cd(L)][NO_3]_2$, $[Hg(L)][ClO_4]_2$, and $[Pb(L)][NO_3]_2$ were prepared as described previously [7,8] and spectra obtained from solutions in either dimethyl sulphoxide–methanol (1 : 1) or dimethyl sulphoxide alone, with concentrations of the order of, or greater than, 1.0 mol dm^{-3} (for exact concentrations see Table). Aqueous solutions (10% D_2O) of the cydta^{4-} complexes with concentrations of between 0.5—0.7 mol dm^{-3} were prepared as for the earlier ^{13}C n.m.r. studies.[6]

The ^1H-decoupled ^{15}N n.m.r. spectra were measured at natural abundance with a Bruker WH180 F.T. spectrometer (at P.C.M.U., Harwell) operating at 18.24 MHz and employing 25-mm diameter n.m.r. tubes. Deuteriated solvents [99% (^2H)] provided the lock signal, and the temperatures were monitored and held constant (±4.0 °C) with a standard Bruker control unit. This rather large

^{15}N N.m.r. chemical shifts [a] and $^{1}J(M-^{15}N)$ values

Compound	Concentration/ mol dm^{-3}	Temperature/ K	δ/p.p.m.	$^{1}J(M-^{15}N)$/Hz	Scans/ 1 000
$[Pb(cydta)]^{2-}$	0.5	303	−312.3	187.5	28
$[Cd(cydta)]^{2-}$	0.5	298	−341.5	80.9 83.8	34
$[Ag(cydta)]^{3-}$	0.5	295	−345.2		29
$[Hg(cydta)]^{2-}$	0.7	295	−329.1	365.7	27
$[Hg(Hcydta)(OH)]^{2-}$	0.5	298	−331.2	395.5	27
$[Hg(Hcydta)Cl]^{2-}$	0.5	295	−328.8	388.7	27
$[Cd(L)][NO_3]_2$ [b]	0.9	233	−344.8 −349.7	75.0 125.0	9 9
$[Cd(L)][NO_3]_2$ [c]	0.9	233	−348.2	110.0	9
$[Pb(L)][NO_3]_2$ [d]	0.9	303	−318.8 −325.5 −11.8	207.5 19.8	20 20 20
$[Hg(L)][ClO_4]_2$	1.7	253	−335.8	317.7	2
cydta^{4-}, pH = 12	0.7	298	−344.4		7
pH = 7	0.7	298	−339.4		7
L	1.0	295	−344.9		0.571

[a] Relative to $Me^{15}NO_2$ at δ = 0. [b] Trigonal-bipyramidal structure. [c] *trans*-III Structure. [d] Ref. 8.

estimated uncertainty in the temperature is a consequence of the use of 25-mm sample tubes. Spectral widths varied from 600 to 12 000 Hz depending upon the desired Hz–point resolution, and all free induction decays were stored in 8K data points. A pulse angle of *ca.* 30° was used with no delay between successive acquisitions. Chemical shifts are reported in p.p.m. referenced to external ^{15}N-nitromethane at $\delta = 0$. The nuclear Overhauser enhancement of the $[Hg(cydta)Cl]^{3-}$ ion was measured by standard gated decoupling techniques.

RESULTS AND DISCUSSION

The spectra of the cydta^{4-} complexes all display single sharp inverted resonances which, despite the absence of any directly bound protons to the nitrogen nuclei, exhibit the near maximum theoretical nuclear Overhauser enhancement {measured for the $[Hg(cydta)Cl]^{3-}$ ion as -3.5 compared to the theoretical maximum of -3.9}, and allow the easy recognition of metal satellite peaks. The observation of single resonances for all these complexes is in accord with the ^{13}C n.m.r. data from a previous study;[6] the symmetry of the sexidentate complexes makes the nitrogen nuclei equivalent, whilst for the quinquedentate complexes of mercury(II) [predominantly axial substitution by X ($X = Cl^-$ or OH^-)],[6] rapid exchange of X^- ion between equivalent sites on the metal again leads to an equivalencing of the nitrogen resonances. A typical spectrum is that of the $[Cd(cydta)]^{2-}$ ion shown in Figure 1.

The spectra obtained for the complexes of 1,4,8,11-tetra-azacyclotetradecane (L) with mercury and lead ions show one and two inverted resonances respectively, corresponding to planar and folded sets of nitrogen-donor atoms as reported previously.[7,8] Whereas the nitrate resonance of $[Cd(L)][NO_3]_2$ was not observed, a small positive peak at -11.8 p.p.m. was recorded for $[Pb(L)][NO_3]_2$. This is attributable to the greater number of scans recorded for the lead complex (Table). The nitrate resonance is small and positive as expected for a nucleus experiencing no nuclear Overhauser enhancement.

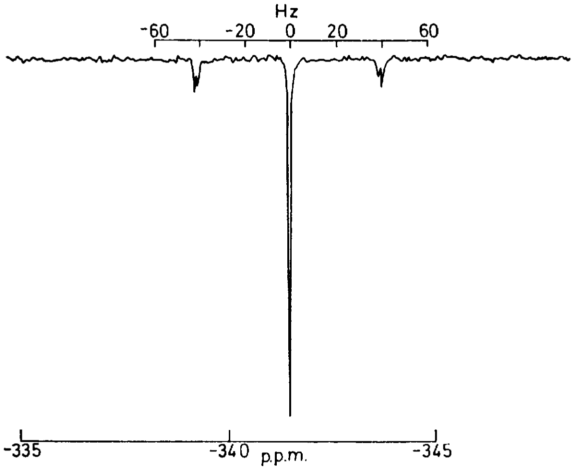

FIGURE 1 ^{15}N n.m.r. spectrum of $[Cd(cydta)]^{2-}$ showing both sets of satellite peaks from ^{111}Cd and ^{113}Cd

We have shown, *via* variable-temperature ^{13}C n.m.r. spectroscopy,[7] that two dynamic processes occur in solutions of $[Cd(L)][NO_3]_2$: a low-energy process with rate constant k_1 whereby two equivalent folded, trigonal-bipyramidal species interconvert by passage through a square-pyramidal intermediate, and a high-energy process, rate constant k_2, at elevated temperature involving the interconversion of two species possessing planar sets of nitrogen donors of configurations *R,S,S,R* and *R,S,R,S*. These processes are summarised in Figure 2. The variable-temperature ^{15}N n.m.r. spectra of this compound fully support our previous conclusions; at 233 K the spectrum contains three resonances, and as the temperature is increased, two of these collapse to a single line at 293 K and further increase in temperature results in the incipient collapse at 353 K of the remaining two resonances (see Figure 3). The resonance at 345.1 p.p.m. which appears at 293 K can, therefore, be assigned to the complex in a time-averaged square-pyramidal conformation, and the two resonances (-344.8 and -349.7 p.p.m.) which collapse to yield this new resonance assigned to axial and equatorial N donors of a trigonal-bipyramidal species, both of these species having the N-donor configurations *R,S,R,S*. The resonance at -348.2 p.p.m. which remains unchanged throughout the temperature range 233—333 K is assigned to the species with a planar set of nitrogen atoms of configuration *R,S,S,R* (also known as the *trans*-III isomer).[7] All of these resonances exhibit different one-bond metal–nitrogen spin couplings, and are discussed in detail below.

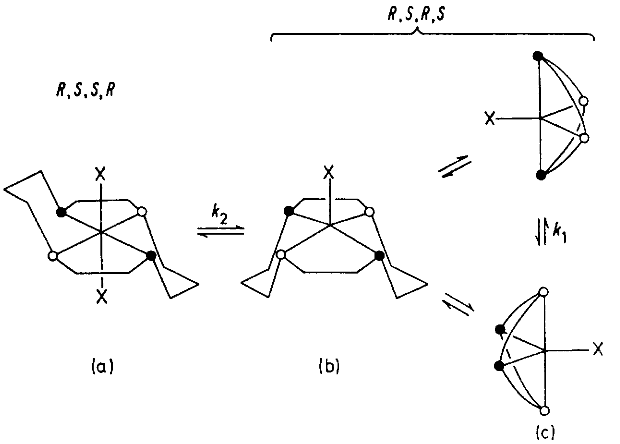

FIGURE 2 Dynamic equilibria between *R,S,S,R* (*trans*-III isomer) and *R,S,R,S* nitrogen-donor configurations of L for $[Cd(L)][NO_3]_2$ (X = nitrate ion or solvent molecule)

Chemical Shifts.—The chemical-shift data presented in the Table show that there is either very little change or only a slight movement towards low field for the ligand chemical shifts on co-ordination. This tendency towards a low-field co-ordination shift matches that observed by Roberts and co-workers[2] for cadmium and mercury complexes of the ethylenediaminetetra-acetate ion (edta^{4-}), but is in the opposite direction to the co-ordinate shift recently observed for complexes of alkyldiamines with rhodium.[3] Our findings also differ from an earlier ^{14}N study of ethylenediamine with cobalt which showed co-ordination shifts to high field of the free ligand.[9]

Nuclear magnetic shielding is conventionally discussed in terms of Saika and Slichters's (atomic) approximation of Ramsey's (molecular) formalism,[10] where the total screening $\sigma(A)$ of a nucleus, A, is expressed as the algebraic sum of a local diamagnetic term ($\sigma_d{}^A$), a local paramagnetic term ($\sigma_p{}^A$), and a third term $\Sigma\sigma^{AB}$ to account for the effects of other atoms within the molecule, and include medium effects [equation (1)]. For

$$\sigma(A) = \sigma_d{}^A + \sigma_p{}^A + \Sigma\sigma^{AB} \qquad (1)$$

nuclei other than protons, $\Sigma\sigma^{AB}$ is often neglected and assumed to be of minor importance in determining the overall shielding, whilst $\sigma_d{}^A$ is considered to change little from compound to compound.[11] Chemical-shift discussions, therefore, often centre on factors influencing $\sigma_p{}^A$, although variations in σ_d are sometimes allowed for by use of an approximation intermediate between that of Slichter and Ramsey in which the nearest neighbours are included in the σ_d and σ_p terms.[2,12] In this way, Roberts and co-workers calculated a large increase in the value of $\sigma_d{}^A$ for complexed edta^{4-} ion *versus* the free ligand.[2] However, to rationalise the small downfield shifts that they observed, they postulated a similarly large increase in $\sigma_p{}^A$ upon complex formation, effectively cancelling the change in $\sigma_d{}^A$ and yielding a small net shift. In view of the near cancellation of opposing effects it is very difficult to propose an unequivocal shift mechanism for the complexes studied here.

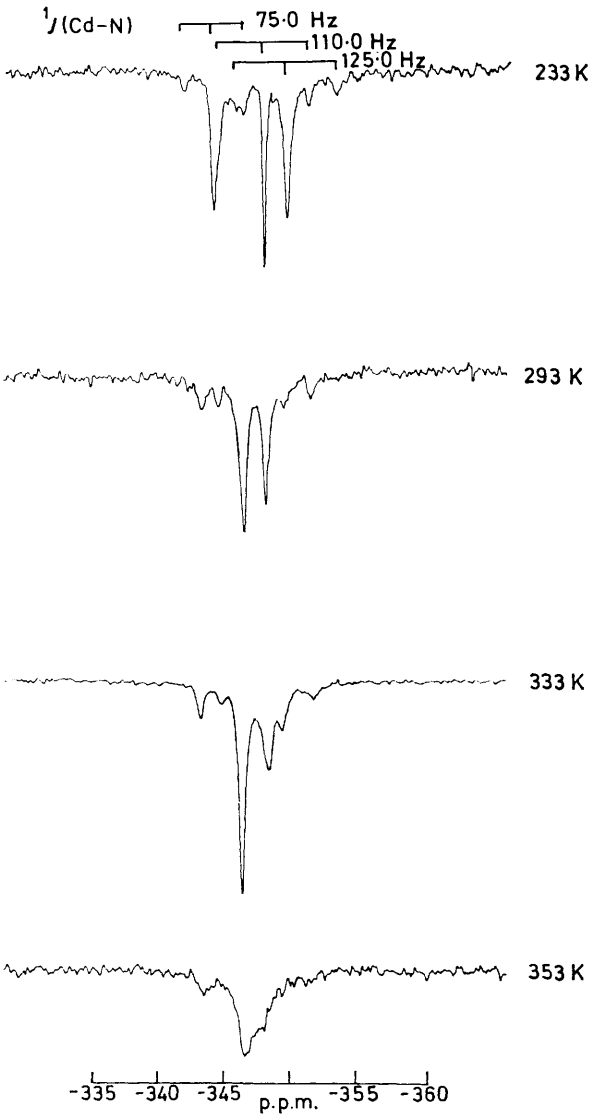

FIGURE 3 Variable-temperature ^{15}N n.m.r. spectra of [Cd(L)][NO$_3$]$_2$ [0.9 mol dm^{-3} in methanol–dimethyl sulphoxide (1 : 1)]

Coupling Constants.—All the metal nuclei used in this study possess magnetically active isotopes of nuclear spin $\frac{1}{2}$; cadmium possesses two, ^{111}Cd (13%) and ^{113}Cd (12%). As a result, all the spectra except those observed for the silver complexes give rise to metal satellite peaks. It proved very easy to obtain ^1J(M–^{15}N) from the cydta^{4-} complexes, and these have been taken as typical values for the metals in strain-free octahedral environments, and are included in the Table. The spectrum of [Cd(cydta)]$^{2-}$ ion allowed the resolution of both sets of satellites from ^{111}Cd and ^{113}Cd and the ratio of the observed couplings (80.9 Hz : 83.3 Hz), 0.97 : 1, is in good agreement with the ratio of the isotope magnetogyric ratios $^{111}\gamma : {}^{113}\gamma = 0.96 : 1$, as expected. These couplings are also very close to the average ^1J values of 81 Hz noted for the edta^{4-} complex.[2] For mercury(II) the edta^{4-} complex yielded no coupling information, due to rapid ligand exchange; however, the greater inertness of the cydta^{4-} complex enabled couplings to be measured for both the sexidentate complex [Hg(cydta)]$^{2-}$, 365.7 Hz and quinquedentate complexes [Hg(Hcydta)X]$^{2-}$, 395.5 Hz (X$^-$ = OH$^-$) and 388.7 Hz (X$^-$ = Cl$^-$). The increase of *ca.* 6% in the coupling constant for [Hg(Hcydta)X]$^{2-}$ ions implies a slight strengthening of the metal–nitrogen bonds as a consequence of binding the anionic group X and may possibly be due to electrostatic repulsion between X and the acetate ions, leading to a decrease in the strength of metal bonds through O, accompanied by a compensatory increase in the strength of bonds through N. There is some evidence to support this explanation from earlier ^{13}C studies [6] which showed small two-bond carbon to metal couplings through O for the quinquedentate species compared with the sexidentate species.

The only previous value of ^1J(Pb–^{15}N) reported (261 Hz) was that obtained from a double-resonance experiment for 95% ^{15}N-enriched [PbMe$_3$(NMePh)].[4] This value is not too dissimilar to the coupling of 187.5 Hz measured for the [Pb(cydta)]$^{2-}$ ion.

The silver(I) complex of cydta^{4-} ion did not show any coupling to ^{15}N in agreement with the absence of couplings to ^{13}C observed in a previous study.[6] This was attributed to greater ionic character for the ligand–metal bond for silver(I) compared with cadmium(II), mercury(II), and lead(II). This might also partly explain the near coincidence of the cydta^{4-} chemical shifts for free ligand and the silver(I) complex.

The Complex $[Pb(L)][NO_3]_2$.—For the complexes of L, significant differences were observed between the one-bond metal couplings of the two resonances due to folded macrocycle species.[8] The two resonances observed for $[Pb(L)][NO_3]_2$ display very different ^1J(Pb–N) of 207.5 and 19.8 Hz. From the theoretical expression for spin coupling devised by Pople and Santry,[13] which for the coupling between two nuclei A and X in the absence of π bonding can be written as (2) where α^2 represents the

$$^1J \propto \alpha_A^2\alpha_X^2\psi_A^2(0)\psi_X^2(0)\Delta E^{-1} \quad (2)$$

percentage *s* character of the relevant hybrid bonding orbital, $\psi^2(0)$ is the valence *s* electron density at the nucleus, and ΔE is the singlet–triplet excitation energy, the great disparity in the coupling implies very different modes of bonding to the two N sites. The *X*-ray crystal structure of the complex [8] has shown it to approximate to *cis*-octahedral geometry but with considerable distortion from the ideal for the nitrogen positions. A stereochemically active lead lone pair forces the nitrates to participate in principally ionic bonding to the metal in an asymmetrically bidentate fashion. For regular O_h geometry the equatorial N–Pb–N bond angle of 83.3° is almost ideal whilst the axial N–Pb–N bond angle of 134.7° shows considerable distortion. This means that whereas the equatorial nitrogens would be in a favourable position for binding to the hybrid octahedral orbitals of the lead atom, the axial donors are displaced from the ideal positions. Since the Pb–N bond lengths do not reflect any weakening of the axial bonds (the bond lengths are all very similar) and due to the distortion apparent within the structure, it is reasonable to propose a substantial rehybridisation of the lead(II) orbitals, which if it involved even a small change in α_{Pb}^2 or $\psi_{Pb}^2(0)$ could result in vastly different couplings. However, it should be emphasised that Kennedy *et al.*[4] have shown that expression (2) is misleading for interpretations of ^1J(PbX), and concluded that the couplings depend significantly on β_{PbX} the *s*-overlap integrals. Irrespective of the detailed interpretation of ^1J(PbX), if the axial distortion observed in the crystal of $[Pb(L)(NO_3)_2]$ is maintained in solution, it seems reasonable to assign ^1J(PbN) as 207.5 Hz for the equatorial donors and 19.8 Hz for the axial donors, on the perhaps naive assumption that the equatorial bonds approximate to normal 'octahedral' hybridisation.[8] This implies that 207.5 Hz may be regarded as 'normal' for a lead–nitrogen one-bond coupling, and is in line with our value of 187.5 Hz measured for the $[Pb(cydta)]^{2-}$ ion.

The Complex $[Cd(L)][NO_3]_2$.—If ^1J(Cd–N) for a normal octahedral coupling can be taken as 82.4 Hz {the average value of $^1J(^{111}Cd–N)$ and $^1J(^{113}Cd–N)$ for $[Cd(cydta)]^{2-}$} the value of 110 Hz measured for the *trans*-III species [see Figure 2(a)] of $[Cd(L)][NO_3]_2$ appears anomalous. However, this increase in the coupling probably reflects the constrictive effect of the macrocycle and the consequent compression of the Cd–N bond distance. For the trigonal-bipyramidal species, the difference between the couplings to the equatorial and axial nitrogen donors is not as great as that observed for the folded lead complex. Known crystal structures of trigonal-bipyramidal molecules exhibit shorter equatorial bonds (*ca.* 0.1 Å shorter) than axial bonds for d^{10} metal ions.[14] On this basis, the larger coupling of 125.0 Hz can be assigned to the equatorial nitrogens and the smaller coupling of 75.0 Hz to the axial sites. This assignment also coincides with that expected from consideration of the dsp^3 hybridisation scheme of trigonal-bipyramidal molecules which yields axial hybrid orbitals of largely d_{z^2} and p_z character, whilst the equatorial hybrid orbitals have more *s*, p_x, and p_y character. From these results, it would appear that for ^1J(Cd–N), equation (2) may apply in the same way as it does for ^1J(Rh–N)[3] and ^1J(Pt–N).[15]

The Complex $[Hg(L)][ClO_4]_2$.—The observed coupling for $[Hg(L)][ClO_4]_2$ of 318 Hz is significantly less than those measured for the mercury(II) complexes with the cydta^{4-} ion which are in the range 365.7—395.5 Hz. This difference is not explicable in terms of the percentage *s* character of the hybrid orbitals for octahedral and square-pyramidal molecules which would predict a larger value for the square-pyramidal species. It may be that, as with lead(II), the mutual polarisability of the valence *s* orbitals and the *s*-overlap integral between mercury and nitrogen [4] are important, and lead to a breakdown of the simple dependence of ^1J(Hg–N) upon α^2 and $\psi^2(0)$.

Conclusions.—The use of ^{15}N n.m.r. spectroscopy at natural abundance in the study of inorganic complexes is now feasible, provided there is access to a high-field spectrometer with large sample volume capability and also that the complex to be studied is moderately soluble. The spectra are easier to interpret than those from ^{13}C n.m.r. spectroscopy, and can provide information not apparent from the latter technique. The disappointingly small and variable nature of the ligand co-ordination shifts render them of little diagnostic value, whereas the metal–nitrogen one-bond couplings demonstrate potential as a source of stereochemical information.

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