A Carbon-13 Nuclear Magnetic Resonance Study of *trans*-1,2-Diaminocyclohexane-*NNN'N'*-tetra-acetate Ion and its Diamagnetic Metal Complexes

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^{13}C 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 studied for the alkali and alkaline-earth metal ions, Ag^{I}, Tl^{I}, the zinc group, Sn^{II}, Pb^{II}, Al^{III}, La^{III}, Co^{III}, and Th^{IV}. The spectra are generally consistent with sexidentate co-ordination by cydta(4-) except at high pH where further species of the type [M(cydta)OH]$^{n-}$ (M = Tl^{I}, Hg^{II}, and Al^{III}) are observed. Species of the type [M(cydta)X]$^{n-}$ are confirmed for M = Co^{III} (X = Cl) and Hg^{II} (X = Cl, Br, NCS, or CN). Tentative structures for the latter species are discussed, and use is made of ^{2}J metal–carbon hyperfine couplings (Hg^{II}, Pb^{II}, Cd^{II}, or Sn^{II}) and of $^{1}J_{CH}$ couplings to give further structural information. In the presence of the univalent cations (including H^{+}) broad temperature-dependent resonances are observed indicating relatively slow nitrogen inversion in the unco-ordinated or partially co-ordinated ligand.

(*trans*-1,2-DIAMINOCYCLOHEXANE-*NNN'N'*-TETRA-ACETATE ion [cydta(4-)] forms more stable complexes than those of ethylenedinitrilotetra-acetate ion [edta(4-)].[1] Its sexidentate complexes are generally believed to have an octahedral structure. However, the experimental evidence for this is limited, and more complex geometries might also be expected with some metal ions, by analogy with known non-octahedral edta complexes.[2]

The differences in behaviour between cydta and edta can be explained in two complementary ways. The first is that the cyclohexane ring limits the available conformations of the free ligand, and hence reduces the loss of entropy upon chelation.[3] The second explanation is an obvious conclusion from molecular models, namely, that in octahedral or near-octahedral metal complexes of cydta, the axial glycinate CH_2 group (out of the N–M–N plane) is severely sterically compressed against the cyclohexane ring methylenes. This will hasten chelate ring closure should cydta temporarily become quinquedentate by detachment of an axial glycinate arm. A similar but appreciably smaller steric repulsion exists for the equatorial arm. Evidence is presented in this paper which confirms this kinetic hypothesis.

The substantial steric compression of the axial glycinate methylene also has a useful effect on the ^{13}C n.m.r. spectrum of all cydta complexes. It shifts that resonance between 3 and 8 p.p.m. upfield, so that it is always unambiguously distinguishable from the equatorial glycinate methylene resonances. This observation, together with the fact that the third type of carbon directly bound to the nitrogen in cydta is CH rather than CH_2, enables the ^{13}C n.m.r. spectra of cydta and its complexes to be far more readily analysed than those of edta and its complexes.[4] However, although all of the compounds studied show this steric shift, this does not prove that they are strictly octahedral. Structures in which the metal ion is, for example, seven-co-ordinate would also retain some compression of the two glycinate methylenes most removed from the N–M–N plane.

The only cydta complex in which the ligand is widely believed by other authors[5] to be quinquedentate is [Co^{III}(cydtaH)Cl]$^{-}$. This only exists for extended periods in strongly acid solution at high [Cl^{-}]. The binding site of the Cl^{-} is thought to be equatorial (in the N–M–N plane). However, other complexes of the type [M(cydta)X]$^{n-}$ (X = unidentate ligand) have been reported in the literature, in which cydta is potentially behaving as a quinquedentate ligand. Examples are Al^{III} (X = OH^{-})[6] and Hg^{II} (X = OH^{-}, Cl^{-}, Br^{-}, I, or SCN^{-}).[7] The existence of these and other complexes is confirmed in the present work and the five-co-ordination of cydta in them is indicated.

Four different structures (other than optical isomers) are possible for octahedral [M(cydta)X]$^{n-}$ species in which the ligand is five-co-ordinate. These are shown below. Two further structures are shown which are distinguishable only if the nitrogen or oxygen atoms are labelled. Structures (II) and (IV) are expected to be sterically strained, particularly with larger cations. Structure (II) involves the generally less-stable meridional co-ordination and structure (IV) involves unfavourable puckering of the cyclohexyl ring. Also, neither structure is directly accessible from the sexidentate complex, by the opening of one chelate ring. We have found no definite n.m.r. evidence for these two structures with any metal–cydta complex, and will therefore follow general practice in not considering them further. Structures of type (I) and (III), however, are both known for edta complexes of Co^{III}.[4,8a] Structure (I) is believed for a variety of good reasons to be the more stable with this metal ion.[9]

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[1] 'Stability Constants,' *Chem. Soc. Special Publs.*, 17 and 25, 1964 and 1971; James D. Carr and D. G. Swartzfager, *Analyt. Chem.*, 1970, **42**, 1238; 1971, **43**, 1520.

[2] J. L. Hoard, G. S. Smith, and M. Lind, in 'Advances in the Chemistry of the Coordination Compounds,' ed. S. Kirschner, Macmillan, New York, 1961, p. 296.

[3] F. L. Garvan, 'Chelating Agents and Metal Chelates,' eds. F. P. Dwyer and D. P. Mellor, Academic Press, New York, 1964, ch. 7.

[4] O. W. Howarth, P. Moore, and N. Winterton, *J.C.S. Dalton*, 1974, 2271.

[5] F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, 1961, **83**, 2610.

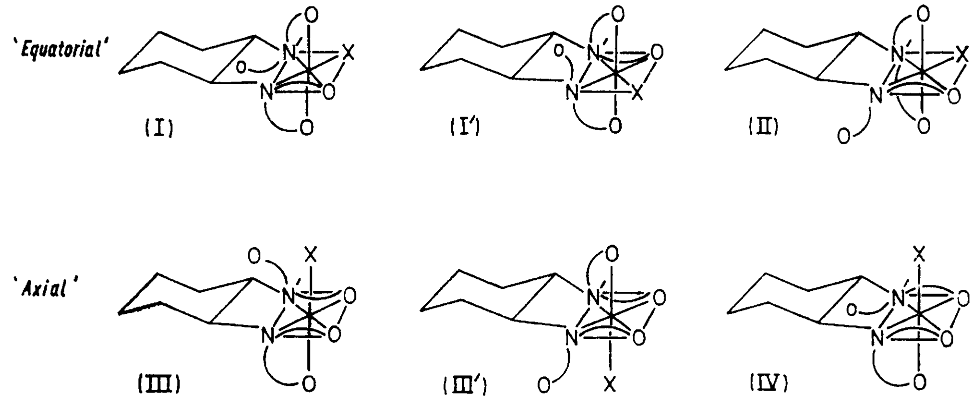
[6] J. Stary, *Analyt. Chim. Acta*, 1963, **28**, 132.

[7] D. L. Jones and D. W. Margerum, *Inorg. Chem.*, 1966, **5**, 1135.

[8] O. W. Howarth, P. Moore, and N. Winterton, (*a*) *Inorg. Nuclear Chem. Letters*, 1974, **10**, 553; (*b*) *J.C.S. Chem. Comm.*, 1974, 664.

[9] H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, 1959, **81**, 549.

There is a variety of distinguishable exchange processes possible for cydta complexes. The most extreme process is that of total ligand exchange. This has been investigated by stopped flow[10] and by proton n.m.r.[11] methods, which have both shown that the exchange is acid catalysed. Complexes range from being totally inert (Co^{III}) through to being labile (*e.g.* most divalent metal ions). Complexes of univalent metal ions are only stable at high pH.[1,11]



A somewhat less extreme exchange process is that in which axial and equatorial glycinate arms interconvert without total ligand removal. With cydta complexes (unlike edta complexes) this interconversion is almost impossible unless at least one nitrogen atom becomes unco-ordinated and hence free to invert and rotate about the CH-N bond.[11,12] The nitrogen-inversion process additionally implies that at least two carboxylate oxygen atoms also become temporarily unco-ordinated. It is highly plausible that the partial ligand exchange which leads to axial–equatorial interconversion of the glycinate arms is kinetically similar to the process of total ligand exchange. We find no reasons for doubting this from the results of the present study, for we only observe axial–equatorial glycinate interconversion under conditions in which total ligand exchange is incipient.

The above two exchange processes are the only ones that will be apparent in the ^{13}C n.m.r. spectra of $[M(cydta)]^{n-}$ in which cydta is totally or predominantly sexidentate. However, more limited exchange processes are detectable if cydta is acting as a quinquedentate ligand. For simplicity we will only consider exchange involving octahedral structures (I) (equatorial substitution) and (III) (axial substitution), although many other non-octahedral structures could be discussed in similar terms. Complex ions with structures (I) or (III) can interconvert by cydta first becoming sexidentate and then opening again at another chelate ring. This process will also interconvert either (I) or (III) with (I') and (III') (in which the substitution occurs on the opposite side of the molecule). We will refer to these processes as (I)–(III), (I)–(I'), and (III)–(III') exchange respectively, and will describe the exchange as rapid if it leads to complete equivalencing of axial (or, separately, equatorial) carbon atoms on the ^{13}C n.m.r. timescale. It should be noted that none of these three processes interchanges axial and equatorial glycinate arms. Exchange of this kind should also generally be acid catalysed. In one case we have also detected catalysis by Tl^+ ion. Rapid (I)–(III), (I)–(I'), or (III)–(III') exchange will yield an n.m.r. spectrum apparently the same as that obtained from a sexidentate complex, and further shift, relaxation or coupling evidence will be required to establish its presence.

(I)–(III) and (I)–(I') Exchange might also occur by a concerted mechanism in which the substituent group (X) never leaves the metal ion. However, we have no evidence for such a process. A third kinetic possibility might involve quadridentate or lower co-ordination, the intermediate being for example $[M(cydta)X_2]^{n-}$. Evidence is presented for such species with Hg^{II} ($X = CN^-$).

EXPERIMENTAL

Materials.—$K[Co^{III}(cydta)]$ was prepared by a published method.[13] It was converted in solution into the ion $[Co^{III}(cydtaH)Cl]^-$ by heating in conc. HCl at 340 K for *ca.* 10 min. After cooling to room temperature 20% conc. ^2HCl was added for a deuterium lock signal. The ^{13}C spectrum (Figure 1) indicates >70% conversion into the chloro-complex. Attempts to prepare the bromo-complex in an analogous way were unsuccessful. Basification of $[Co^{III}(cydtaH)Cl]^-$ also failed to produce a significant concentration of $[Co^{III}(cydta)Cl]^{2-}$, there being a rapid chelate ring closure and return to $[Co^{III}(cydta)]^-$. Selective deuteriation of $[Co^{III}(cydta)]^-$ was carried out by heating in acidified ^2H_2O.[12]

The other complexes (except Na^I and Li^I) were generally prepared in solution by first dissolving $cydtaH_4$ (1/800 mol) in aqueous 5 mol l^{-1} KOH (slightly less than 1/200 mol) and adding it to the finely ground nitrate salt of the metal ion (slightly less than 1/800 mol). 0·25 ml $^2H_2$ (20%) Was added for a deuterium lock signal. Samples

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[10] D. W. Margerum, P. J. Menardi, and D. L. Jones, *Inorg. Chem.*, 1967, **6**, 283; D. W. Margerum, J. B. Pausch, G. A. Nyssen, and G. F. Smith, *Analyt. Chem.*, 1969, **41**, 233; N. R. Larsen and A. Jensen, *Acta Chem. Scand.*, 1973, **27**, 1838.

[11] R. J. Day and C. N. Reilley, *Analyt. Chem.*, 1965, **37**, 1326.

[12] J. L. Sudmeier and C. N. Reilley, *Analyt. Chem.*, 1964, **36**, 1707.

[13] F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, 1959, **81**, 2955.

usually dissolved when stirred, but occasionally it was necessary to dilute with 20% ^2H_2O. The pH was adjusted with a pH-meter by adding drops of 5 mol l^{-1} KOH or HNO_3 as necessary. Small amounts of undissolved material were removed by centrifuge. If a slight excess of free ligand were not present larger precipitates of metal hydroxy-species were sometimes obtained. The Li^I and Na^I complexes were simply prepared by dissolving the free acid in LiOH or NaOH. Complexes of the type $[Hg^{II}(cydta)X]^{n-}$ were either prepared by using HgX_2 instead of $Hg(NO_3)_2$ (X = Cl or Br) or by adding KX to $[Hg^{II}(cydta)]^{2-}$ [prepared from $Hg(NO_3)_2$] (X = I, OH, NCS, or CN). Known equilibrium constants [7] were used to ensure almost complete formation of $[Hg^{II}(cydta)X]^{n-}$. Final concentrations were usually in the range 0·3—1·0 mol l^{-1}. No significant concentration effects upon chemical shifts were observed, which almost certainly rules out the presence of dimeric or polymeric complexes.

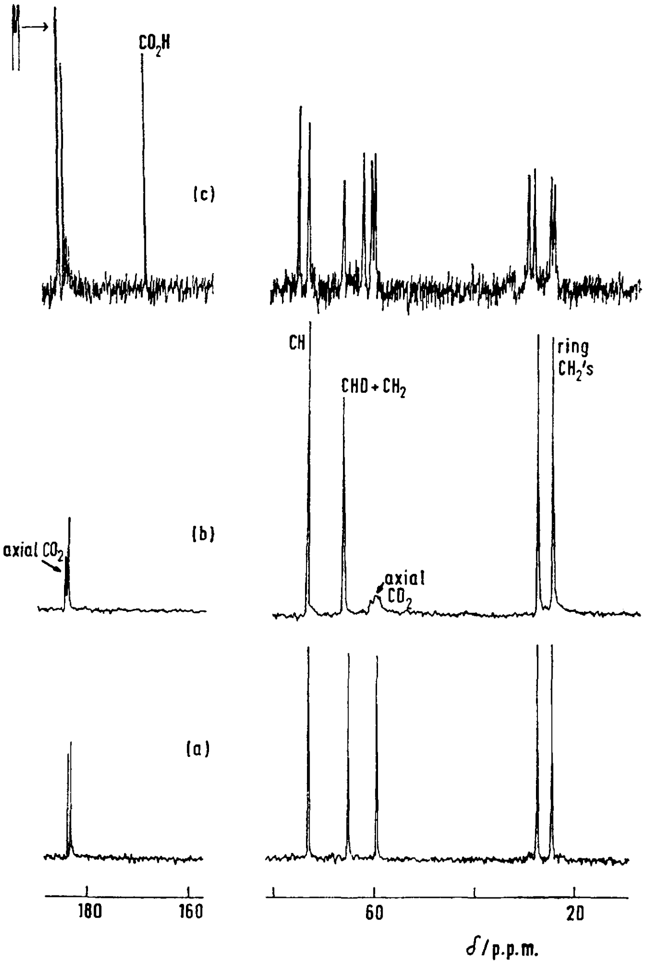

FIGURE 1 ^1H Decoupled ^{13}C n.m.r. spectra of (a) $[Co(cydta)]^-$ (b) $[Co(cydta)]^-$ after total deuteriation of the ' axial ' glycinate CH_2 groups and partial deuteriation of the ' equatorial ' CH_2 groups showing the almost complete absence of the ' axial ' methylene resonance, and a reduction in intensity of the ' axial ' CO_2 resonance) (c) $[Co(cydtaH)Cl]^-$ prepared as described in text followed by saturation of the solution with gaseous HCl at 273 K to decrease the amount of unchanged $[Co(cydta)]^-$

Spectra.—Measurements were made with a Bruker WH90 Fourier Transform spectrometer at a frequency of 22·63 MHz. Broad-band proton decoupling was used where appropriate, a typical accumulation time for 4k data points and 2 000—10 000 fast scans being 8—40 min. Undecoupled spectra, dilute samples, or spectra with wide lines took considerably longer to run (sometimes overnight). Fourier transforms were carried out on 8k data points. It was found necessary to reduce sweep widths to obtain optimum resolution of metal to carbon hyperfine couplings. For example, a typical sweep width of 5 kHz was reduced to 0·5 kHz to investigate the carboxylate region (see Figure 2) or to 1·2 kHz to investigate the methylene region. Linewidths were typically 1—2 Hz(CO_2^-) and 3—4 Hz(CH_2). An external (capillary) TMS standard was used, and the chemical shifts of all but the broadest lines were found to be readily reproducible to within ±0·1 Hz. With undecoupled spectra the lines were broader, because of unresolved long-range couplings, so that the hyperfine $^1J_{CH}$ couplings of even fully separated resonances were only measurable to ±1·5 Hz. Measurements were generally made near ambient temperature (303 K), but lower temperatures were sometimes necessary to reduce exchange, and higher temperatures were used occasionally to sharpen lines or to increase solubility. The temperature coefficients of all the chemical shifts were very similar, being *ca.* +0·02 p.p.m. K^{-1} for CH and CH_2 resonances and +0·01 p.p.m. K^{-1} for CO_2^- resonances.

Selective relaxation of unbound glycinate methylene protons was carried out with the aim of obtaining further structural information. Our general observation is that addition of *ca.* 0·03 mol l^{-1} of Mn^{II} or Gd^{II} selectively reduces the nuclear Overhauser enhancement, and hence the height, of unbound methylene carbon resonances. Mn^{II} (unlike Gd^{III}) Also greatly broadens all CO_2^- resonances at this concentration. The method works best in the pH range 4—12. It was initially tested on the complex $[Co^{III}(edta)Cl]^{2-}$, which is known from other considerations to have structure (I).[4]

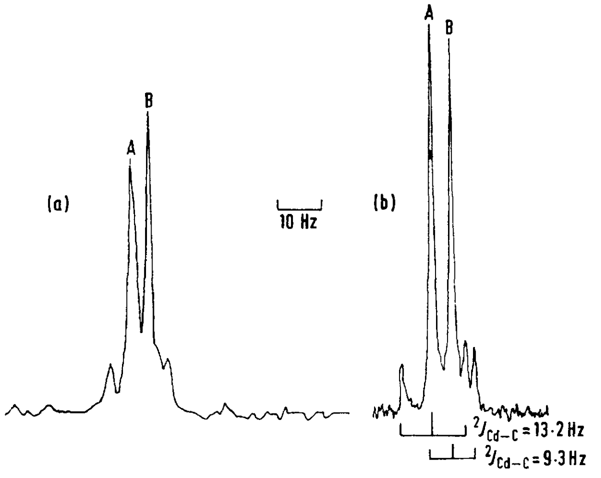

FIGURE 2 Part of the ^1H decoupled ^{13}C n.m.r. spectrum of $[Cd(cydta)]^-$ showing separate $^2J_{Cd-C}$ hyperfine couplings to the two carboxylate resonances (A) and (B). Improved resolution in spectrum (b) was obtained by using a sweep width of 0·25 kHz rather than the usual sweep width of 5 kHz [spectrum (a)]

RESULTS

Our main chemical shifts results are presented in Table 1. Shifts are in p.p.m. downfield of TMS. Direct carbon-to-proton coupling constants at 303 K are reported in Table 2;

TABLE 1

Chemical shifts (p.p.m. from TMS) of compounds studied

Compound	pH	T/K	CO_2^- shift	CH shift	Equatorial CH_2 shift	Axial CH_2 shift	Cyclohexane ring CH_2 shift	Comments
Uncomplexed or protonated cydta	5·2	303	174·0(×4)	64·1(×2)	56·3(×4)		24·4(×2), 25·1(×2)	K^+ salt [a]
	8·4	283	176·2(×4)	62·6(×2)	57·4(×2)	52·7(×2)	25·3(×2), 24·3(×2)	K^+ salt
	9·9	296	175·8(×4) [a]	63·1(×2)	55·1(×4) [f]		25·6(×4)	NMe_4^+ salt
	10·9	273	176·3(×4)	62·4(×2)	57·2(×2)	52·6(×2)	25·2(×2) 24·2(×2)	K^+ salt
	10·9	280	176·0(×4)	62·5(×2)	55·1(×4)		25·5(×2), 24·4(×2)	NH_4^+ salt [a]
	>13	291	181·1(×4)	61·5(×2)	55·9(×4)		26·5(×2), 24·2(×2)	K^+ salt [a]
$[\mathrm{Na^{I}(cydta)}]^{3-}$	>13	270	181·8(×2), 181·5(×2)	61·8(×2)	58·3(×2)	53·6(×2),	26·4(×2), 24·7(×2)	Glycinate broadening at 304 K
$[\mathrm{Li^{I}(cydta)}]^{3-}$	>13	270	182·4(×2), 181·5(×2)	63·3(×2)	59·2(×2)	53·4(×2)	26·2(×4)	Glycinate broadening below pH 9
$[\mathrm{Ag^{I}(cydta)}]^{3-}$	10·7	280	181·3(×2), 180·3(×2)	61·4(×2)	58·5(×2)	54·3(×2)	26·4(×2), 24·6(×2)	Glycinate broadening below pH 9
$[\mathrm{Tl^{I}(cydta)}]^{3-}$	9·6	270	180·6(×2), 179·9(×2)	61·2(×2)	56·2(×2)	52·7(×2)	26·2(×2), 24·9(×2)	Some glycinate broadening
$[\mathrm{Tl^{I}(cydta)OH}]^{4-}$	>13	270	180·5(×3), 179·2	61·4, 61·2	56·9, 55·5	53·3, 51·7	26·2(×2), 25·3, 24·4	Some residual exchange broadening and axial substitution
$[\mathrm{Mg^{II}(cydta)}]^{2-}$	5·2	303	181·4(×2) 181·0(×2)	63·0(×2)	59·6(×2)	54·1(×2)	26·0(×4)	No broadening observed except below pH 4
$[\mathrm{Ca^{II}(cydta)}]^{2-}$	5·2 and 12·5	303	181·5(×2), 181·0(×2)	62·4(×2)	58·9(×2)	54·2(×2)	26·2(×2), 25·0(×2)	No broadening observed except below pH 4
$[\mathrm{Sr^{II}(cydta)}]^{2-}$	5	303	181·4(×2), 181·0(×2)	62·1(×2)	58·7(×2)	54·4(×2)	26·2(×2), 24·7(×2)	No broadening observed except below pH 4
$[\mathrm{Ba^{II}(cydta)}]^{2-}$	8	303	181·4(×2), 181·0(×2)	61·7(×2)	58·4(×2)	54·5(×2)	26·3(×2), 24·3(×2)	No broadening observed except below pH 4
$[\mathrm{Sn^{II}(cydta)}]^{2-}$	11·3	303	178·2(×2) 178·1(×2)	63·3(×2)	57·8(×2)	53·5(×2)	26·1(×2), 25·6(×2)	
$[\mathrm{Pb^{II}(cydta)}]^{2-}$	6·4—>13	307	180·3(×2), 179·9(×2)	63·2(×2)	57·1(×2)	53·1(×2)	26·3(×2), 25·9(×2)	No broadening observed except below pH 4
$[\mathrm{Zn^{II}(cydta)}]^{2-}$	8	303	180·4(×2), 179·8(×2)	66·4(×2)	62·9(×2)	54·6(×2)	26·1(×2), 25·1(×2)	No broadening observed except below pH 4
$[\mathrm{Cd^{II}(cydta)}]^{2-}$	7 and 13	303	179·9(×2), 179·7(×2)	62·5(×2)	58·5(×2)	54·1(×2)	26·2(×2), 25·8(×2)	No broadening observed except below pH 4
$[\mathrm{Hg^{II}(cydta)}]^{2-}$	7	300	178·5(×2) 178·3(×2)	61·8(×2)	57·9(×2)	53·8(×2)	26·0(×2), 25·8(×2)	No broadening observed except below pH 4
$[\mathrm{Hg^{II}(cydta)Cl}]^{3-}$	6	303	177·8(×2), 178·2(×2)	61·3(×2)	57·8(×2)	53·7(×2)	25·9(×2), 25·5(×2)	Predominantly axial substitution [e]
$[\mathrm{Hg^{II}(cydta)Br}]^{3-}$	6	303	177·8(×2), 178·2(×2)	61·3(×2)	57·8(×2)	53·8(×2)	26·0(×2), 25·6(×2)	Predominantly axial substitution [e]
$[\mathrm{Hg^{II}(cydta)I}]^{3-}$	6	303	178·0(×2), 178·3(×2)	61·4(×2)	57·7(×2)	54·0(×2)	26·1(×2), 25·7(×2)	Predominantly axial substitution [e]
$[\mathrm{Hg^{II}(cydta)OH}]^{3-}$	12·6	303	178·0(×2), 178·4(×2)	61·5(×2)	58·1(×2)	54·1(×2)	26·1(×2), 25·5(×2)	Predominantly axial substitution [e]
$[\mathrm{Hg^{II}(cydta)SCN}]^{3-}$	8·3	303	177·7(×2), 178·2(×2)	61·6(×2)	57·9(×2)	53·9(×2)	25·9(×2), 25·5(×2)	Predominantly axial substitution [e]
$[\mathrm{Hg^{II}(cydta)CN}]^{3-}$		303	176·9(×2), 177·9(×2)	61·9(×2)	57·7(×2)	53·5(×2)	25·8(×2), 25·3(×2)	Predominantly axial substitution [e, g]
$[\mathrm{Hg^{II}(cydta)(CN)_2}]^{4-}$		275	177·5(×4) [f]	62·2(×2)	55(×4) [f]		25·4(×2), 24·2(×2)	Predominantly axial substitution [e, h]
$[\mathrm{Al^{III}(cydta)}]^{-}$	2·5—6·0	275	177·2(×2), 176·8(×2)	65·5(×2)	62·6(×2)	54·9(×2)	25·4(×2), 23·3(×2)	50% Conversion at pH 7·8,[e]
$[\mathrm{Al^{III}(cydta)OH}]^{2-}$	9·3—10·7	275	178·0(×2), 177·6(×2)	66·6(×2)	63·5(×2)	54·2(×2)	26·7(×2), 24·9(×2)	equatorial substitution
$[\mathrm{La^{III}(cydta)(H_2O)}_n]^{-}$	8	340	182·0(×2), 181·3(×2)	64·3(×2)	60·6(×2)	55·9(×2)	26·1(×2), 25·4(×2)	Poor solubility
$[\mathrm{Co^{III}(cydta)}]^{-}$	4—10	303	183·7(×2) [d] 183·1(×2)	73·3(×2)	65·1(×2)	59·3(×2)	26·8(×2), 23·8(×2)	
$[\mathrm{Co^{III}(cydtaH)Cl}]^{-}$	conc. HCl	303	185·4,[d] 185·2,[d] 184·3, 168·3 [c]	75·4, 74·0	65·6, 61·7 [c]	59·8, 59·3	28·3, 27·4, 24·9, 24·3	Equatorial substitution [b]
$[\mathrm{Th^{IV}(cydta)(H_2O)}_n]$	1·5	305	182·0(×2), 181·1(×2)	64·3(×2)	60·2(×2)	55·5(×2)	25·5(×2), 25·1(×2)	Species uncertain

[a] Rapid exchange of axial and equatorial glycinates. [b] Shifts corrected for acid medium effect using $[\mathrm{Co^{III}(cydta)}]^{-}$ shifts in the same solution. Observed shifts were: 186·5, 186·4, 185·5, 169·9, 75·3, 73·7, 66·6, 62·6, 60·8, 60·1, 29·0, 27·9, 24·8, 24·2. [c] Unco-ordinated glycinate. [d] Axially bound carboxylate. [e] Rapid (I)–(III), (I)–(I′), and/or (III)–(III′) exchange. [f] Incipient splitting, hence very broad. [g] Bound CN^- at $\delta = 147·1$ p.p.m. at 275 K. [h] Exchanging CN^- at $\delta = 153·1$ p.p.m. at 275 K.

fully resolved splittings are ±1·5 Hz, other splittings (±3 Hz) are in parentheses. Direct metal-to-carbon hyperfine couplings, where found, are reported in Table 3. These couplings were virtually independent of temperature, in the absence of exchange processes. Results in parentheses are ±0·3 Hz.

Some representative spectra are shown in Figures 1—3.

DISCUSSION

Shifts.—Every spectrum studied was readily analysable into carboxylate peaks, methine carbons, equatorial and axial glycinate methylenes, and cyclohexyl methylenes. The chemical shifts observed are fully consistent with those that would be predicted by standard empirical methods. However, it was not generally possible to assign the individual carboxylate peaks as axial or equatorial (except with Co^{III} and Hg^{II}) because axial–equatorial glycinate exchange precluded selective deuteriation experiments. The cyclohexyl methylene carbon resonances were also in general close to each other, and in the free ligand were shown to reverse their shift order around pH 9. The reason for this near-coincidence of shifts is that the downfield shift of *ca.* 8 p.p.m. expected for the methylene carbons β to tertiary nitrogen is almost exactly offset by the same upfield steric compression shift [14] as is observed with the axial glycinate methylene carbons. For this reason we have made no further attempt to identify the cyclohexyl resonances.

TABLE 2

$^1J_{CH}$ Values at 303 K (in Hz)

Compound	pH	$^1J_{CH}$ (axial glycinate)	$^1J_{CH}$ (equatorial glycinate)	$^1J_{CH}$ (methine)	Goldschmidt ionic radius/pm
Free $cydta^{4-}$	>13	135 [a]		137	
$[Li^I(cydta)]^{3-}$	>13	133	134	(129)	78
$[Tl^I(cydta)]^{3-}$	5·8	143 [a]		145	149
$[Tl^I(cydta)OH]^{4-}$ [d]	12·6	136	(132) [b]	(134)	149
$[Mg^{II}(cydta)]^{2-}$	5·2	137	(132)	(132)	78
$[Ca^{II}(cydta)]^{2-}$	12·5	136	(134)	*c*	106
$[Sr^{II}(cydta)]^{2-}$	5	136	(136)	(137)	127
$[Ba^{II}(cydta)]^{2-}$	8	134	137	*c*	143
$[Cd^{II}(cydta)]^{2-}$	7	136	138	*c*	103
$[Hg^{II}(cydta)]^{2-}$	6	136	138	(140)	93
$[Hg^{II}(cydta)OH]^{3-}$	13	137	139	(139)	93
$[Hg^{II}(cydta)I]^{3-}$	6	137	139	(141)	93
$[Pb^{II}(cydta)]^{2-}$	11·5	138	137	137	117
$[Al^{III}(cydta)]^{-}$	5·8	141	142	144	45
$[Al^{III}(cydta)OH]^{2-}$	10·1	140	140	139	45
$[Co^{III}(cydta)]^{-}$	8	142	145	143	

[a] Rapid axial–equatorial glycinate exchange. [b] All results in parentheses ±3 Hz, otherwise ±1·5 Hz. [c] Not reliably measurable owing to unfavourable overlapping. [d] At 270 K.

The detailed chemical shifts observed are closely consistent with those obtained for edta complexes,[4] and are therefore also adequately explained by the arguments of Roberts *et al.*[15] The large upfield shifts in $[Co^{III}(cydta)]^{-}$, and even more so in $[Co^{III}(cydtaH)Cl]^{-}$, are attributable to temperature-independent paramagnetism.[4] Unfortunately, the shifts of the free ligand are sufficiently similar to those of the fully bound ligand (in all cases except Co^{III}) that chemical shifts alone are inadequate to identify the resonances of unco-ordinated carboxylate or glycinate carbons. The identifications reported in Table 1 are therefore made on the basis of selective broadening, and those in Table 3 on the basis of selective broadening (in part) and of metal–carbon hyperfine coupling constants.

$^1J_{C-H}$ Couplings.—Substantial evidence already exists that the $^1J_{C-H}$ couplings of chemically comparable ring CH_n groups correlate directly with the angle strain at the carbon concerned.[16,17] This contention is borne out in general by the results in Table 2, although additional effects cannot be fully excluded. The glycinate methylene couplings are *ca.* 136 Hz both in the free ligand and in most of the metal complexes. Higher couplings and hence greater chelate ring strain are apparent in $[Co^{III}(cydta)]^{-}$, $[Al^{III}(cydta)]^{-}$, and $[Tl^I(cydta)]^{3-}$. Co^{III} and Al^{III} Have the smallest ionic radii of those metals studied, and Tl^I the largest. The strain appears to be released throughout the whole ligand as it becomes quinquedentate $\{[Al^{III}(cydta)OH]^{2-}$ and $[Tl(cydta)OH]^{4-}\}$. In contrast to this, the ligand in the M^{2+} and Li^+ complexes appears to be relatively unstrained. Where differences between the axial and the equatorial glycinate couplings are apparent the equatorial couplings and hence strains are greater. This is consistent with predictions made on the basis of *X*-ray structures of edta complexes.[2,9]

Unco-ordinated Ligand and Alkali-metal Complexes.—The Li^+ and Na^+ ions form stable complexes ($\log K_1 =$ 6·11 and 4·66 respectively) and at pH 14 and 270 K the clear separation of two resonances both for the carboxylate and for the glycinate methylene groups shows that axial–equatorial glycinate interconversion is rela-

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[14] G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley, New York, 1972, p. 43.

[15] R. Hagen, J. P. Warren, D. H. Hunter, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1973, **95**, 5712.

[16] D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, 1967, **89**, 6612.

[17] D. M. Grant and B. V. Gheyney, *J. Amer. Chem. Soc.*, 1967, **89**, 5315.

tively slow. The chemical shifts of these complexes also differ slightly from those of the unco-ordinated ligand.

In contrast, the K^+ (log K_1 = 1·83), NH_4^+ and tetramethylammonium salts show similar shifts and very rapid axial–equatorial interconversion even at high pH. However, in the pH range 8—13 these salts also display a reduced rate of axial–equatorial interconversion, so that at 270 K the separate methylene resonances are clearly resolved albeit still broadened. Quantitative kinetic measurements on the exchange processes will be reported in a later paper; our preliminary observations are that the exchange is appreciably slower than would be expected for a simple inversion at nitrogen, and is virtually independent of pH within the range 8—11. This pH range corresponds to monoprotonation of cydta (pK_4 = 13·2, pK_3 = 6·2).[1] Our observations are difficult to reconcile with simple successive protonation at nitrogen, but are consistent with a species $(cydtaH)^{3-}$ in which a proton (or hydroxonium ion) is chelated at least by the two nitrogens. A similar conclusion was reached from ^1H n.m.r. studies.[12] The implication of this tentative model is that the slowing of the nitrogen inversion is due to the difference in energy between the symmetrical chelated and the simple unsymmetrical species in which the proton only interacts with one nitrogen atom; only the latter can undergo nitrogen inversion.

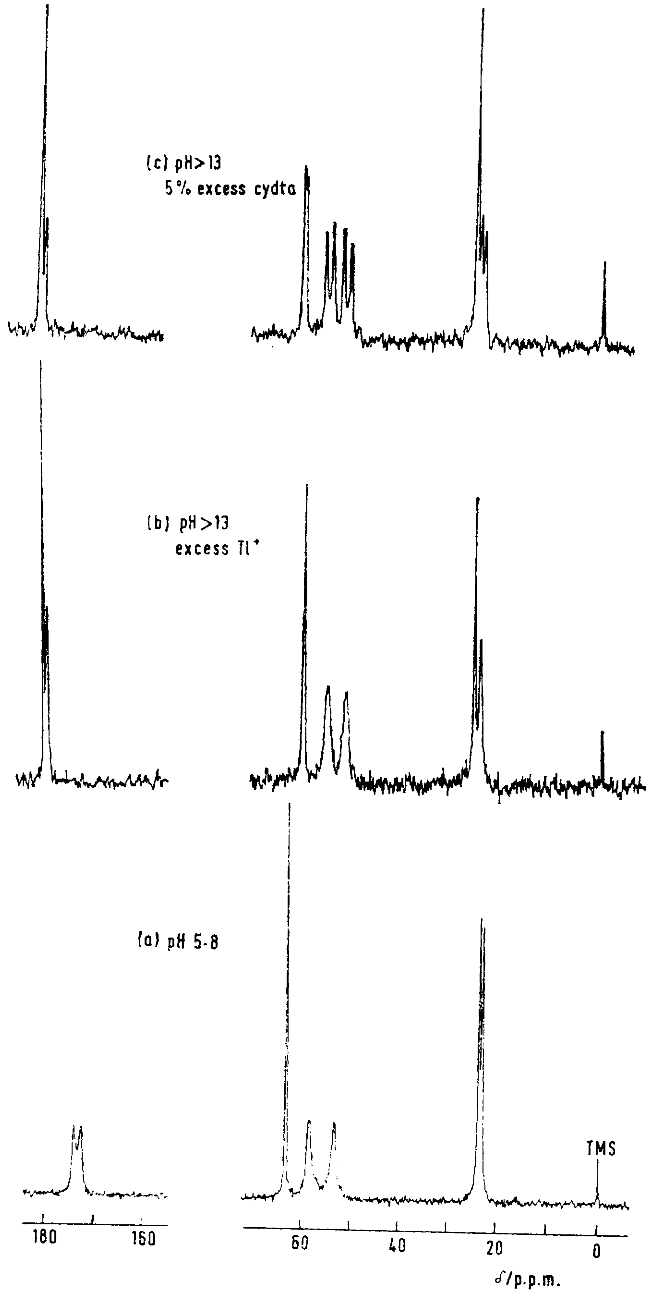

FIGURE 3 ^1H Decoupled ^{13}C n.m.r. spectra of thallium(I) complexes of cydta at 270 K: (a) pH 5·8 – $[Tl(cydta)]^{3-}$; (b) pH >13 and a small excess of Tl^I present; (c) pH >13 and a small excess of cydta present –$[Tl(cydta)OH]^{4-}$

The NH_4^+ salt was prepared in aqueous ammonia solution (*d* 0·880), and the NH_3 present also appears to speed up the axial–equatorial exchange process, possibly by base-catalysed proton transfer.

Silver and Thallium Complexes.—We found, as expected from the stability constants (Ag^I, log K_1 = 8·2; Tl^I, log K_1 = 6·7) [1] that these complexes begin to form above pH 8. By pH 9·5 they only show axial–equatorial glycinate exchange at room temperature, and give sharply separate pairs of carboxylate and glycinate methylene peaks below 280 K. The chemical shifts at *ca.* pH 9·5 are not unlike those of the Na^+ complex, and even in the slow exchange limit the spectra show no sign of hyperfine coupling to either isotope of Ag^I or Tl^I. This is in contrast to Cd^{II}, Hg^{II}, Pb^{II}, and Sn^{II}, and implies that hyperfine coupling to the metal ion is only observed in the presence of strong and probably partly covalent bonding. A similar conclusion was reached from a ^1H n.m.r. study.[11]

The shifts of the Ag^I complex are not significantly pH-dependent above pH 9, and selective relaxation experiments reveal no unco-ordinated carboxylates at pH 12·5. We therefore formulate it as sexidentate $[Ag^I(cydta)]^{3-}$.

In contrast, the spectrum of the Tl^I complex (Figure 3) is strikingly pH-dependent. Although at pH 9·6 its spectrum is very like that of the Ag^I complex at pH 13·0 it shows 11 separate resonances, indicating a loss of the sexidentate C_2 symmetry and suggesting substitution at one co-ordination site by OH^-. As the pH is increased through the range 9·6—13 the peaks mostly split symmetrically, although the δ = 180·6 carboxylate and the δ = 26·2 cyclohexyl methylene peaks do not split detectably. The only unsymmetrical splitting is that of the axial glycinate methylene, in which the δ = 51·7 peak shifts further upfield than expected. This is consistent with its being the unco-ordinated glycinate methylene, sterically compressed against the cyclohexyl ring. Axial substitution is confirmed by selective relaxation; the two right-hand glycinate peaks are halved in intensity on the addition of Mn^{II}

at 0·03 mol l^{-1} and at pH 13. At this pH there is still some residual broadening owing to continuing (III)–(III′) exchange, which helps to explain why both axial glycinate methylene peaks are equally broadened. Presumably the remaining (III)–(III′) exchange is still sufficiently rapid to prevent the build-up of proton saturation on the temporarily co-ordinated axial methylene.

The kinetics of (III)–(III′) exchange have an unexpected feature. At pH 13 and 270 K the exchange is catalysed by the presence of a small excess of $\mathrm{Tl^I}$ ions; if a small excess of free ligand is not present, cooling only broadens those peaks that are fully split in the presence of the excess of cydta. This indicates a substantial rate increase in the presence of $\mathrm{Tl^I}$. It is possible that the free $\mathrm{Tl^I(H_2O)}_n$ ion co-ordinates loosely to the unco-ordinated carboxylate group and also to the bound $\mathrm{OH^-}$ ion, and thus assists in the process of reformation of the sexidentate species. Further ring opening of the sexidentate species gives either structure (III) or (III′), and hence overall (III)–(III′) exchange occurs.

Group IIA Complexes.—$\mathrm{Mg^{II}}$, $\mathrm{Ca^{II}}$, $\mathrm{Sr^{II}}$, and $\mathrm{Ba^{II}}$ Complex strongly with cydta to give complexes which have very similar chemical shifts, independent of pH over the entire range studied. This is consistent with reported stability constants (log K_1 between 8·6 and 11·0).[1] The cydta chemical shifts and $^1J_{\mathrm{CH}}$ couplings in the series fit an octahedral structure in which, as the metal ionic radius increases, the equatorial glycinate rings become more strained, with the equatorial glycinate methylene being increasingly compressed against the cyclohexyl ring so as to lower the equatorial methylene, the methine, and the ring chemical shifts.

Complexes of Divalent Tin, Lead, Zinc, Cadmium, and Mercury.—The spectra of the divalent metal-ion complexes of Groups IIB and IVB all have seven peaks (apart from hyperfine metal–carbon couplings). Although the spectrum of the $\mathrm{Hg^{II}}$ species under alkaline conditions is pH-dependent, those of the $\mathrm{Cd^{II}}$ and $\mathrm{Pb^{II}}$ species are not. This almost certainly indicates that only one $\mathrm{Cd^{II}}$ and $\mathrm{Pb^{II}}$ species is present. Also, because of the similarity of the axial and equatorial $^2J_{\mathrm{M-C}}$ couplings (Table 3), we believe that all four glycinates are co-ordinated in these species, to give sexidentate octahedral co-ordination at all pH values.

Shifts in the $\mathrm{Sn^{II}}$ species are also pH-independent except at very high pH.[18] A selective relaxation experiment at pH 11·3 gave negative results, suggesting that the ligand is sexidentate.

The metal–carboxylate couplings are much larger for $\mathrm{Hg^{II}}$ than for $\mathrm{Cd^{II}}$ or $\mathrm{Pb^{II}}$. This contrasts with the known $^1J_{\mathrm{MC}}$ couplings in $\mathrm{Cd(CH_3)_2}$ and $\mathrm{Hg(CH_3)_2}$, which are comparable in magnitude.[19] Insofar as metal–carbon couplings are attributable to covalent bonding between the metal ion and the donor atoms the indication is that in cydta complexes covalent bonding is substantial for $\mathrm{Hg^{II}}$, less for $\mathrm{Cd^{II}}$ and $\mathrm{Pb^{II}}$, and low for $\mathrm{Tl^I}$ and $\mathrm{Ag^I}$, for which no couplings are, in fact, resolvable.

The apparent differences in $^2J_{\mathrm{M-CO_2^-}}$ between $\mathrm{Pb^{II}}$ and $\mathrm{Cd^{II}}$ may be misleading; the axial and equatorial $\mathrm{Cd^{II}}$ carboxylate peaks are very close together, and may well be in the reverse chemical shift order from those in the $\mathrm{Pb^{II}}$ complex.

The couplings to $\mathrm{Cd^{II}}$, $\mathrm{Hg^{II}}$, and $\mathrm{Pb^{II}}$ may be compared with the results for the corresponding edta complexes.[4] With $[\mathrm{Cd^{II}(edta)}]^{2-}$ an averaged $^2J_{\mathrm{M-CO_2}}$ coupling of 12·1 Hz was observed and with $[\mathrm{Hg^{II}(edta)}]^{2-}$ an averaged coupling of 35 Hz. With $[\mathrm{Pb^{II}(edta)}]^{2-}$ no coupling was resolvable at pH 6. The complete equivalencing of the axial and equatorial glycinates observed with edta complexes is a clear demonstration of the fact that in edta but not in cydta complexes it is easy to interconvert axial and equatorial glycinates without breaking either of the metal to nitrogen bonds.

As the pH was increased above 13, the $\mathrm{Sn^{II}}$–cydta complex, unlike the others, showed rapid axial–equatorial glycinate exchange, and chemical shifts which moved towards those expected for the unco-ordinated ligand. We conclude that a stannite species is formed at high pH in preference to any chelated species.

$[\mathrm{Hg^{II}(cydta)X}]^{3-}$ *Complexes.*—$[\mathrm{Hg^{II}(cydta)}]^{2-}$, Despite its high thermodynamic stability (log $K_1 = 32·7$),[1] has been reported to react with the ligands $\mathrm{X^-}$ [X = Cl, Br, I, NCS, and OH] to give complexes of general formula $[\mathrm{Hg^{II}(cydta)X}]^{3-}$.[7] These complexes are readily investigated by our techniques, which yield the following general information.

(i) Selective relaxation (X = Br or OH) indicates that these complexes are axially substituted by $\mathrm{X^-}$ with cydta acting as a quinquedentate ligand. This rules out, for example, the possibility of a pentagonal bipyramidal structure with all carboxylates co-ordinated.

(ii) All the species observed have C_2 symmetry on the ^{13}C n.m.r. timescale. This implies rapid (I)–(I′), (III)–(III′), and (I)–(III) exchange. However, this exchange is sufficiently slow when $\mathrm{X^-} = \mathrm{CN^-}$ to give broadening of the axial glycinate $\mathrm{CH_2}$ resonance and also to give separate peaks for bound $\mathrm{CN^-}$ ($\delta = 147·1$) and free $\mathrm{CN^-}$ ($\delta = 145·6$) at 275 K.

(iii) The smooth gradation of chemical shifts and couplings through the series indicates that the members all have similar structures (with the possible exception of $\mathrm{CN^-}$ complexes).

(iv) The direction of change of all the shifts upon substitution is opposite to that observed for $\mathrm{OH^-}$ substitution on $[\mathrm{Al^{III}(cydta)}]^-$, which we believe is equatorially substituted (see below). This supports the contention that all the complexes are predominantly axially substituted.

(v) As predicted by the formation constants at high concentration the complexes are almost completely formed provided at least a two-fold excess of $\mathrm{X^-}$ is used. Even in the chloro-complex, no shift or coupling

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[18] F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, 1971, **10**, 1511.

[19] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

differences were observed between a solution in which the excess of Cl^- was two-fold and one in which it was three-fold.

(vi) However, shifts and couplings intermediate between $[Hg^{II}(cydta)]^{2-}$ and $[Hg^{II}(cydta)Cl]^{3-}$ were observed when no excess of Cl^- was present. Extrapolation of the data indicates that the chemical shift order of axial and equatorial carboxylates reverses between these two complexes, and that the signs of the coupling constants do not.

Inspection of the couplings in Table 3 shows that $^2J_{Hg-C}$ couplings *via* oxygen predominate. We identify as axial the carboxylate peak whose coupling is most sharply reduced when an Hg–O bond is broken.

A rather approximate calculation may be carried out, with the simplifying assumption that the $^{199}Hg-^{13}CO_2^-$ couplings are governed entirely by two factors of coupling through oxygen by the three bound carboxylates, and general (non-stereospecific) reduction of this coupling through oxygen due to the covalent binding of X to Hg. The only remaining variable in this simplified model is the percentage of structure (III) present in the dynamic mixture of quinquedentate isomers, which, calculated on this basis increases from 54 to 91% between OH^- and CN^-.* The increase in percentage of axial substitution through the series also approximately parallels the reported formation constants, the ' softness ' of X^-, and the non-stereospecific reduction factor *x*.* A small pH-dependence of the NCS^- isomer ratio is observed.

TABLE 3

Metal–carbon hyperfine couplings (in Hz)

Compound	pH	$^2J_{M-CO_2-}$ Upfield peak	$^2J_{M-CO_2-}$ Downfield peak	Equatorial $^{2,3}J_{M-CH_2}$	Axial $^{2,3}J_{M-CH}$	Methine $^{2,3}J_{M-CH}$	Reported $\log_{10}K$ [c]	Calculated [d] % structure (III)
$[Sn^{II}(cydta)]^{2-}$	11·3	*a*	*a*	(21)	(12)	*b*		
$[Pb^{II}(cydta)]^{2-}$	11·5	12·7	9·2	(13)	*b*	*b*		
$[Cd^{II}(cydta)]^{2-}$	7	9·3 [e]	13·2 [e]	*b*	*b*	*b*		
		equatorial [f]	axial [f]					
$[Hg^{II}(cydta)]^{2-}$	7	40·2	38·2	13·2	24·9	21·5		
$[Hg^{II}(cydta)Cl]^{3-}$	6	29·6	23·4	8·3	22·2	13·9	2·16	64
$[Hg^{II}(cydta)Br]^{3-}$	6	26·5	18·3	*b*	(19)	(13)	3·20	73
$[Hg^{II}(cydta)I]^{3-}$	6	20·6	13·7	*b*	(15)	(12)	5·3	76
$[Hg^{II}(cydta)OH]^{3-}$	12·6	25·8	23·4	*b*	(20)	*b*	3·20	54
$[Hg^{II}(cydta)SCN]^{3-}$	8·3	24·2	20·2	7·7	18·6	9·9	4·29	60
$[Hg^{II}(cydta)SCN]^{3-}$	12	25·4	18·6	*b*	*b*	*b*	—	69
$[Hg^{II}(cydta)CN]^{3-}$	*ca.* 9	19·6	10·6	*b*	*b*	*b*	—	91

[a] Not detected because of poor signal-to-noise ratio. [b] Not detected because $J <$ linewidth. [c] For $[Hg^{II}(cydta)]^{2-} \rightleftharpoons [Hg^{II}(cydta)X]^{3-}$. [d] Approximate result; see text under Hg^{II} heading. [e] Average of couplings to ^{111}Cd and ^{113}Cd. [f] Average of bound and unbound couplings.

We finally note that cyanide ion is unique in the Hg^{II} series studied because if it is added in excess a second species is formed. The relatively broad lines in this species are consistent with the more rapid axial–equatorial interconversion that would be expected with a substituted quadridentate complex.

Al^{III} *Complexes*.—Although a seven-line spectrum is observed at all pH values with Al^{III}, there is a marked change in all the peak positions between pH 7 and 9. This is consistent with other observations of hydroxy-species,[6] and also with our observation that no selective relaxation occurs at pH 5·8, whereas at pH 10 the equatorial glycinate methylene resonances are selectively reduced in intensity both by 0·03 mol l^{-1} Mn^{II} and Gd^{III}. Equatorial substitution is also consistent, as noted in the previous section, with the observation that the changes of all the chemical shifts of the complex upon substitution by OH^- are opposite to the changes with Hg^{II}.

The observed rapid (I)–(I′) exchange in $[Al^{III}(cydta)OH]^{2-}$ is, at first sight, surprising. Whereas in the corresponding edta complex almost all the exchange is slowed on the ^{13}C n.m.r. timescale at pH 9·6 and 270 K,[4] in the cydta complex it is still so fast under these conditions that the seven-line spectrum only shows slight broadening of the axial methylene peak. The likely explanation of the rapid exchange is the fact that in a complex in which cydta is quinquedentate the unco-ordinated glycinate arm of the ligand is more limited in its possible conformation than in a comparable edta complex. This reduces the entropy loss upon reco-ordination, and thus speeds the return to a sexidentate structure. The increase in the rate constant for reco-ordination is also reflected in the observation that the logarithmic formation constant of $[Al^{III}(cydta)OH]^{2-}$ from $[Al^{III}(cydta)]^-$ is 1·7 units lower than for the corresponding edta species.[20]

At very high pH (>13), $[Al^{III}(cydta)OH]^{2-}$ behaves like $[Sn^{II}(cydta)]^{2-}$, giving free ligand plus an aluminate species.

We attempted to make species such as $[Al^{III}(cydta)CN]^{2-}$ by adding an excess of cyanide ion to $[Al^{III}(cydta)]^-$ at neutral pH. However, we found no evidence of any substitution reaction.

We have also carried out a few ^{27}Al magnetic resonance measurements at 22·63 MHz on the cydta and edta

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* If the observed axial coupling in $[Hg(cydta)X]^{3-}$ is *a* Hz and equatorial coupling is *e* Hz, then the non-stereospecific fractional reduction in coupling is $x = [1 - (a/38{\cdot}2 + e/40{\cdot}2)]$, and the percentage axial substitution is $100[2 - a/19{\cdot}1(1 - x)]$, *e.g.* if $X = I$, $a = 13{\cdot}7$, $e = 20{\cdot}6$ (Table 3). Hence $x = 0{\cdot}42$ and therefore the complex is 76% axially substituted.

[20] D. A. Aikens and F. J. Bahbah, *Analyt. Chem.*, 1967, **39**, 646.

complexes of aluminium. The lines obtained are very broad, with widths increasing steadily from 1 to 2 kHz as the pH is increased from 3 to 10. The lower widths at lower pH may probably be ascribed to the higher symmetry of the sexidentate complex. Because of the large line-widths it is not possible to obtain very accurate chemical shifts. The observed peaks are all *ca.* 20 p.p.m. upfield from (capillary) $[Al(H_2O)_6]^{3+}$.

Co^{III} *Complexes.*—Much evidence already exists to show that the complex ion $[Co^{III}(cydta)]^-$ is sexidentate, octahedral, and totally inert at normal temperatures except in very strong acid or base. Our results confirm this; the shifts have already been discussed. We were able to take advantage of the inertness in carrying out selective acid-catalysed deuteriation of the axial glycinate protons. The resulting compound showed only a very small broad peak at $\delta = 183{\cdot}7$ p.p.m., thus confirming our assignments of the axial peaks (Figure 1).

The same axially deuteriated complex was converted into $[Co^{III}(cydtaH)Cl]^-$ by dissolution in conc. HCl/^{2}HCl (see Experimental section). This permitted assignment of some of the 14 peaks observed with the undeuteriated chloro-complex (Figure 1) at $\delta = 59{\cdot}8$, 59·3, 185·4, and 185·2 as arising from axial glycinates. As the unco-ordinated carboxylate must (in acid solution) give the peak at $\delta = 168{\cdot}3$, this proves that $[Co^{III}(cydtaH)Cl]^-$ has structure (I). The resonance at $\delta = 61{\cdot}7$ p.p.m. is almost certainly that of the unco-ordinated equatorial glycinate methylene; a similar lowering of δ at low pH was observed with the corresponding peak in the edta complex.[4] We found no evidence for the formation of any aqua-complex from $[Co^{III}(cydta)]^-$ in 8 mol l^{-1} $HClO_4$. $[Co^{III}(edtaH)H_2O]$ Is formed under similar circumstances from $[Co^{III}(edta)]^-$.[4] This is evidence that rapid ring closure occurs with $[Co^{III}(cydtaH)H_2O]$ but not with $[Co^{III}(cydtaH)Cl]^-$, from which the aqua-complex can presumably be transiently formed.[5]

Lanthanum and Thorium Complexes.—There are several reasons for expecting the complexes between La^{III} or Th^{IV} and cydta to be more than six-co-ordinate. One of these grounds is the observation that several bidentate chelates, including tiron(4−) [tiron(2−) = 1,2-dihydroxybenzene-3,5-disulphonate ion] can complex readily with $[Th^{IV}(cydta)(H_2O)_n]$ to give 1 : 1 adducts.[1] Another is the relatively high solubility of the uncharged Th^{IV} complex.

Our observations on the Th^{IV} complex at pH 1·5 suggest a symmetric sexidentate complex (on the n.m.r. timescale). If any carboxylates were unco-ordinated at this pH then, even with (I)–(I′) or (III)–(III′) exchange, the mean carboxylate chemical shifts would be considerably less. The similarity of the Th^{IV} and La^{III} shifts to those found for other metal complexes is a clear demonstration of the insensitivity of the cydta shifts to variations in the charge on the central metal ion.

Upon addition of an equimolar quantity of Na$_2$tiron to the Th^{IV} complex followed by adjustment to pH 4, broad lines are observed. These are presumably broad due to intermediate-rate exchange of tiron. They narrow, without shifting significantly, as the pH is increased to 9·5. At this higher pH the spectrum shows no lines attributable either to free cydta, $[Th^{IV}(cydta)(H_2O)_n]$, or to free tiron. However, it does show the presence of two major species approximately in 2 : 1 ratio. The differences in shift between these species (typically 0·5 p.p.m.) is more than one could reasonably expect from a simple 180° reversal of the (unsymmetrically substituted) tiron moiety. In view of the large number of stereochemically possible species, we will not hazard structural guesses for these two species, although we note that they must have sufficient stereochemical differences not to interconvert rapidly on the n.m.r. timescale at pH 9·5.

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