Carbon-13 Nuclear Magnetic Resonance Study of Propane-1,3-diamine-*NNN'N'*-tetra-acetate Ion and its Diamagnetic Metal Complexes

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Diamagnetic metal complexes of propane-1,3-diamine-*NNN'N'*-tetra-acetate ion (pdta^{4-}) have been studied by ^{13}C n.m.r. spectroscopy. The results confirm previous studies in showing that complexes in which the ligand is quinquedentate are not formed (except possibly with Hg^{II}), but also show that this is due not to decreased ring strain in the six-co-ordinate complexes but rather to steric compression of the glycinate chelate arms arising from the bunched backbone methylene groups. At low pH the complex formed between pdta^{4-} and Al^{III} is more inert than the analogous ethylenediamine-*NNN'N'*-tetra-acetate (edta^{4-}) complex despite the lower equilibrium formation constant, and this is in line with the reduced tendency of pdta^{4-} to form complexes in which the ligand is quinquedentate.

CARBON-13 n.m.r. spectroscopy has already proved to be a powerful technique for investigating the structures, steric strains, and exchange dynamics of the diamagnetic metal complexes of multidentate ligands such as ethylenediamine-*NNN'N'*-tetra-acetate ion (edta^{4-}) [1,2] and *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate ion (cydta^{4-}).[3,4] The present study compares these results with observations on complexes of propane-1,3-diamine-*NNN'N'*-tetra-acetate ion (pdta^{4-}) in order to investigate the effects of introducing an extra methylene group into the ethylenic backbone of edta^{4-}. Previous work indicates that in complexes of pdta there is a lowering of the formation constants (except for small metal ions where the stability constants are similar to those of edta [5]), an increase in the rate of partial ligand exchange (so as to permit inversion at nitrogen [6]), and a disfavouring of species in which pdta is acting as a quinquedentate rather than a sexidentate ligand.[7] The lowering of the stability constants compared with edta is mainly attributable to a loss of enthalpy of binding, rather than to entropy differences; this is in contrast to complexes of cydta, where the main conformation of the free ligand is close to that required for chelation, so that the net entropy gain on chelation is increased.

Our results confirm these earlier observations, and show that the largest effect determining the differences is not relief of chelate ring strain but rather is steric compression arising from the bunching of the six-membered 'backbone' chelate ring. Although complexes of pdta in which the ligand is sexidentate are strongly favoured, we present evidence for the presence of other complexes with Hg^{II}.

EXPERIMENTAL

Materials.— Propane-1,3-diamine-*NNN'N'*-tetra-acetate was synthesised by the method of Weyh and Hamm.[7] ^{13}C N.m.r. spectra showed the absence of any major impurities. The salt K[Co^{III}(pdta)] was prepared directly by a published method [8] and also by the reaction between $K_3[Co(NO_2)_6]$ and pdta, using a procedure which for the edta complex gives [9] K_2[Co^{III}(edta)(NO_2)]. Other metal complexes were prepared from the metal nitrates or perchlorates in solution in water (plus 20% ^2H_2O for a lock signal) by dropwise addition of Na[OH] until the correct pH was

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[2] O. W. Howarth, P. Moore, and N. Winterton, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 553.

[3] O. W. Howarth, P. Moore, and N. Winterton, *J.C.S. Dalton*, 1975, 360.

[4] O. W. Howarth, P. Moore, and N. Winterton, *J.C.S. Chem. Comm.*, 1974, 664.

[5] 'Stability Constants of Metal–Ion Complexes,' *Special Publ.* Nos. 17 and 25, The Chemical Society, London, 1964 and 1971.

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[7] J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, 1968, **7**, 2431.

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reached. Final concentrations were in the range 0.3—1.0 mol dm^{-3}; no significant concentration effects were observed.

Spectra.—Measurements were made with a Bruker WH 90 spectrometer by previously published methods.[1,3] The temperature dependences, as with cydta,[3] were *ca.* 0.01 p.p.m. K^{-1} for CO_2^- resonances and 0.02 p.p.m. K^{-1} for CH_2 resonances.

RESULTS AND DISCUSSION

Our main chemical-shift results are presented in Table 1, in p.p.m. downfield of $SiMe_4$. The shifts are generally similar to those observed with edta [1] and cydta,[3] with the exceptions noted below. $^1J_{CH}$ Values for selected compounds are recorded in Table 2.

TABLE 1

Chemical shifts (p.p.m. from $SiMe_4$) of compounds studied

Compound [a]	pH	T/K	δ/p.p.m. CO_2^{-} [b]	δ/p.p.m. 'Glycinate' [b] CH_2	δ/p.p.m. Backbone CH_2–N	δ/p.p.m. Backbone CH_2–C	Comments
L^{4-}	14	307	180.7	60.2	54.4	24.1	K^+ salts
HL^{3-}	7.7	307	173.4	59.1	54.4	21.5	
$[MgL]^{2-}$	9.25	314	180.5	63.3	58.5	24.1	Broadening of all peaks at pH <7
$[CaL]^{2-}$	14	316	181.2	63.5	62.1	24.8	
$[SrL]^{2-}$	9	313	180.3	62.4	59.6	24.0	
$[ZnL]^{2-}$	5.2	310	179.8	63.3	60.2	24.4	
$[CdL]^{2-}$	13	305	178.9	61.2	59.7	24.7	No couplings to Cd detected
$[HgL]^{2-}$	6.4	285	176.0	61.2	56.9	30.3	
$[Hg(CN)L]^{3-}$ (?) [c]	10.9	276	177.3	61.6	60.0	23.3	Plus equimolar K[CN]
$[HgClL]^{3-}$ (?)	8.9	283	176.2	60.9	58.2	24.0	Some line broadening
$[PbL]^{2-}$	7.7	305	180.4	61.6	59.5	24.7	No couplings to ^{207}Pb detected; broadening at pH <6
$[AlL]^-$	1.9—8	285	176.8 175.7	65.9 59.7	53.0	20.6	
$[CoL]^-$	8—10	310	182.4 [d] 180.7 [e]	69.2 [d] 61.9 [e]	50.8	20.2	

[a] L^{4-} = pdta^{4-}. [b] Rapid exchange of axial and equatorial glycinate arms except for Co^{III} and Al^{III}. [c] Bound CN^- at δ 145.1 p.p.m., *cf.* free CN^- at 168.5 p.p.m. [d] 'Axially' bound glycinate arms. [e] 'Equatorially' bound glycinate arm.

TABLE 2

$^1J_{CH}$ Values at ambient temperature

Compound	pH	J/Hz Glycinate CH_2	J/Hz Backbone CH_2–N	J/Hz Backbone CH_2–C
L^{4-} [a]	14	134	132	124
HL^{3-}	7.7	143	142	128
$[CoL]^-$	1	145 [b] (143) [c]	(142)	132
$[AlL]^-$	7	(143) [b,c] 144	(148) [c]	(127) [c]
$[HgL]^{2-}$	6.4	140 [d]	(142) [c]	129
$[Hg(CN)L]^{3-}$	10.9	138 [d]	*e*	*e*

[a] L^{4-} = pdta^{4-}. [b] Equatorial methylene. [c] Figures in parentheses are ±3 Hz, otherwise ±1.5 Hz. [d] Rapid exchange of axial and equatorial glycinate arms. [e] Not reliably observable.

Uncomplexed Ligand.—The increase in $^1J_{CH}$ on protonation is consistent with the initial protonation being at nitrogen, but not at oxygen.

Mercury Complexes.—The high δ value for the central backbone methylene is surprising, and probably reflects a small change in geometry imposed by the covalent contribution to the ligand binding. That this contribution is larger than with edta and cydta, especially for bonding of nitrogen, is apparent from the $^2J_{C-Hg}$ couplings which were observed. These couplings (in Hz) are 41.5 (38.2, 40.2) for carboxylate carbons, 35.2 (24.9, 13.2) for glycinate methylene carbons, and 33.5 (21.5) for outer backbone methylene carbons, where the figures in parentheses are those observed for the [Hg^{II}(cydta)]$^{2-}$ ion for comparison. It may be noted that the couplings are observed {as with the carboxylate couplings in [Hg^{III}(edta)]$^{2-}$} even in the presence of rapid axial–equatorial ligand arm exchange, which shows that this exchange does not involve total ligand removal.

The couplings disappeared, however, on addition of equimolar amounts of chloride or cyanide ions, or above pH 8. In addition, substantial shifts were observed, especially with the central backbone methylene carbon. These shifts are not all in the direction expected for simple rapid exchange between [Hg^{II}(pdta)]$^{2-}$ and free ligand. Therefore there must be additional species present. However, these species are appreciably more labile than the corresponding species obtained from [Hg^{II}(cydta)]$^{2-}$, and may therefore be a dynamic mixture containing other than a quinquedentate ligand. Evidence for the disfavouring of the quinquedentate form comes from an additional experiment in which the cyano-complex was re-acidified to pH 6.3. The resulting spectrum had almost sharp peaks corresponding to [Hg^{II}(pdta)]$^{2-}$ plus separate rather broad peaks with shifts and widths not unlike those observed[3] for [Hg^{II}-(CN)$_2$(cydta)]$^{4-}$. The addition of acid appears to favour disproportionation of the complex in which pdta is mainly five-co-ordinate, which clearly illustrates the relative disfavouring by pdta of species in which the ligand is quinquedentate.

It has been proposed [7,10] on the basis of models that pdta has appreciably less ring strain than edta when bound to 2+ and 3+ metal ions. However, an *X*-ray study of the [Co^{III}(pdta)]$^-$ ion [11] shows that the net ring

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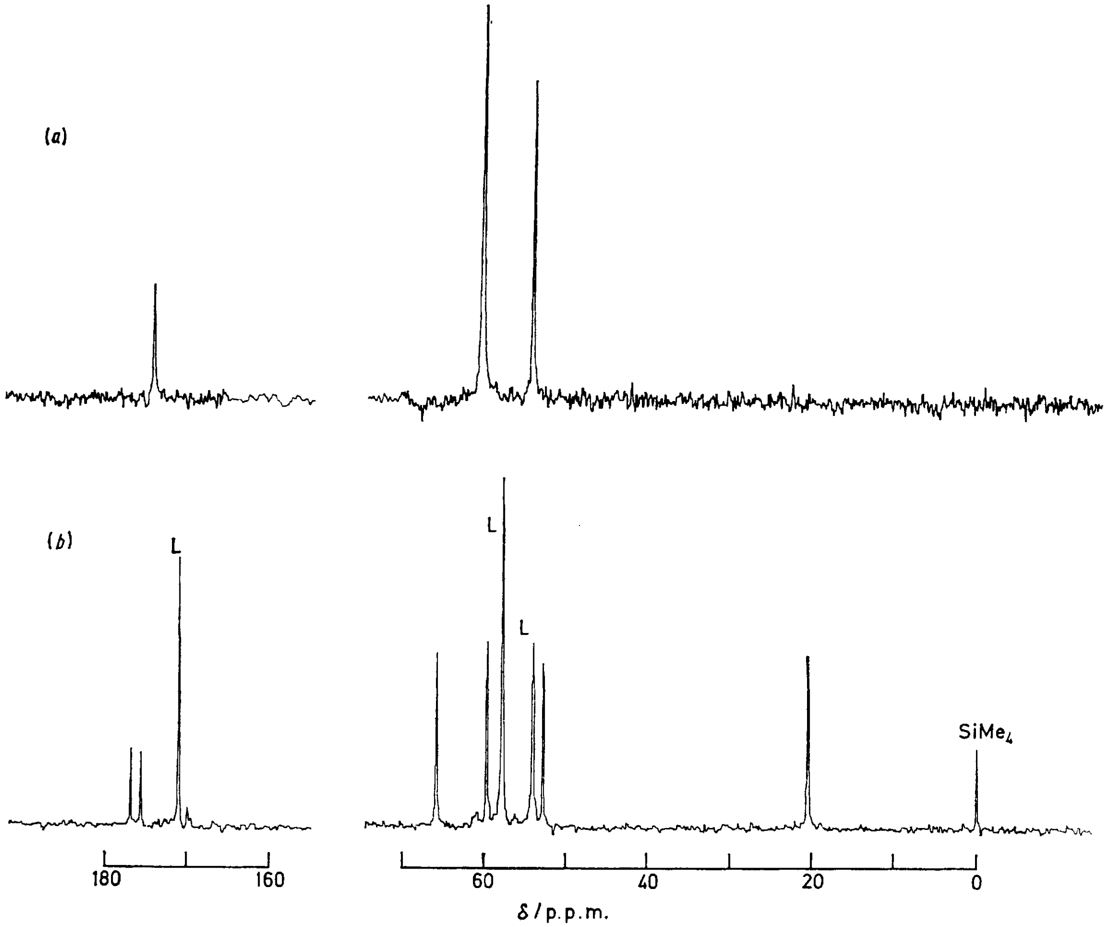
[11] R. Nagao, F. Marumo, and Y. Saito, *Acta Cryst.*, 1972, **B28**, 1852; L. J. Halloran, R. E. Caputo, R. D. Willett, and J. I. Legg, *Inorg. Chem.*, 1975, **14**, 1762.

strains are comparable. Model-compound studies[12] have shown that ring strain can be readily detected in ^{13}C n.m.r. spectra from the variation of $^1J_{CH}$ for carbon atoms in the ring; $^1J_{CH}$ increases by up to 30% in highly strained molecules. Increases of *ca.* 5% were observed with cydta complexes of Al^{III} and Co^{III}, with the largest increases being, as expected, in the equatorial chelate rings.[3] With pdta (Table 2) comparable increases were observed. This suggests that the ring strains are similar in pdta and cydta complexes.



Comparison of the 22.628-MHz ^1H-decoupled ^{13}C n.m.r. spectra (at 285 K) of: (*a*) Al^{III} and edta at pH 2.4; and (*b*) Al^{III} and pdta at pH 1.9. L denotes resonances of uncomplexed ligand

Complexes of Al^{III} *and* Co^{III}.—In contrast to edta and cydta, the aluminium(III) and cobalt(III) complexes of sexidentate pdta show no tendency whatever to ring-open partially to give complexes in which the ligand is quinquedentate. Furthermore, the rate of overall ligand loss is slower, because at pH 1.8 the $[Al^{III}(pdta)]^-$ ion co-exists with free pdta while showing no detectable exchange in the ^{13}C n.m.r. spectrum, even at 350 K. In contrast, under the same conditions, the $[Al^{III}(edta)]^-$ ion shows rapid exchange with no detectable broadening of the ^{13}C resonances.[1] This difference in lability between the $[Al(edta)]^-$ and $[Al(pdta)]^-$ ions is illustrated in the Figure. Since there is no significant exchange broadening of the ^{13}C resonances in either spectrum, one can estimate that the rate constants for ligand exchange are $>10^3$ s^{-1} for $[Al(edta)]^-$ and <0.1 s^{-1} for $[Al(pdta)]^-$. Exchange rates at these upper and lower limits would lead to a 50% increase in the linewidths in the limits of fast and slow exchange respectively, which would have been easy to detect. As the initial rates of complex formation by edta and pdta are known to be very similar,[6] the reduced rate of total exchange is probably due once again to the disfavouring by pdta of a structure in which the ligand is quinquedentate. Such a structure is an unavoidable intermediate in the process of overall complex formation.

We propose that the disfavouring of a structure in which pdta is quinquedentate is caused primarily by steric compression between the bunched backbone methylenes and the glycinate methylenes and carboxylates. The presence of this compression is confirmed by the large (6 p.p.m.) shift difference between 'axial' (out of the N–M–N plane) and 'equatorial' (in-plane)

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[12] K. Wüthrich, S. Meiboom, and L. C. Snyder, *J. Chem. Phys.*, 1970, **52**, 230; K. L. Servis, W. P. Weber, and A. K. Willard, *J. Phys. Chem.*, 1970, **74**, 3960.

glycinate methylene carbons in both the aluminium(III) and the cobalt(III) complexes of pdta; the 6 p.p.m. upfield shift of the axial glycinate methylene resonance is very similar to that found at carbons 3 and 5 in the axial conformer of methylcyclohexane,[13] in steroids,[14] and in sugars.[15] Similar steric compression of axial glycinate methylenes was also detected in cydta complexes [3] and, much less markedly (*ca.* 1 p.p.m. upfield), in edta complexes.[1] *X*-Ray studies [11,16] show that even in the $[Co^{III}(edta)]^-$ ion steric crowding, especially of the axial chelate rings, is not insignificant. In the $[Co^{III}(pdta)]^-$ and $[Co^{III}(cydta)]^-$ ions it is severe. The crowding also helps to explain related observations, such as the tendency of the cobalt(III) and rhodium(III) complexes of 3,7-diazanonane-1,9-diamine to adopt the *trans* configuration.[17]

Selective base-catalysed deuteriation of the axial glycinate methylenes by the method of Sudmeier and Occupati [18] was carried out to establish the peak assignments of the $[Co^{III}(pdta)]^-$ ion (Table 1). The assignments closely follow those for the $[Co^{III}(cydta)]^-$ ion, with the ' axial ' methylenes being more compressed than the ' equatorial '. The deuteriation rate of the ' axial ' glycinate methylenes was faster than in the $[Co(edta)]^-$ ion and was similar to that observed for the $[Co(cydta)]^-$ ion.[18-20] This enhancement has also been attributed to steric compression which favours deprotonation in the transition state. Conversely, the ' equatorial ' methylene protons of the $[Co^{III}(pdta)]^-$ ion were completely inert even at pH 12.4; this opposite effect confirms the presence of considerable strain in the equatorial glycinate rings, which disfavours methylene deprotonation.

There was no evidence in the spectra for the presence of more than one symmetrical conformation of the backbone methylene on the n.m.r. time scale. One further minor difference in the complex of Co^{III} was that acidification produced upfield ' solvent ' shifts more than twice as large as those observed with edta or cydta. It appears that at pH <1 the complex is protonated loosely and generally, even though it is not ring-opened and thus protonated specifically.

[5/2051 *Received*, 20*th October*, 1975]

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