Use of Selective ^{1}H Relaxation in a ^{13}C Nuclear Magnetic Resonance Study of (*trans*-Cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetato)hydroxothallium(I)

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Summary A ^{13}C n.m.r. study at 270 K indicates the formation of $[\text{Tl}^{\text{I}}(\text{cdta})\text{OH}]^{4-}$, cdta = (cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetate)$^{4-}$ from $[\text{Tl}^{\text{I}}(\text{cdta})]^{3-}$ at high pH, and the addition of small amounts of paramagnetic $[\text{Mn}^{\text{II}}(\text{cdta})]^{2-}$ aids in the assignment of an axial structure by selectively broadening the two axial of the four observed resonances from the acetate CH_2 groups.

trans-1,2-Diaminocyclohexane-*NNN'N'*-tetra-acetate ion is well known for its ability to form highly stable metal complexes with the majority of metal ions including thallium(I).[1] Complexes of the type $[\text{M}(\text{cdta})\text{X}]^{n-}$ in which cdta^{4-} acts as a quinquedentate ligand (with one acetate arm unco-ordinated) are also reported[1,2] for M = Hg$^{\text{II}}$ (X = Cl, Br, I, NCS, OH) and when X = OH for a number of metal ions of charge greater than +1 (*e.g.*, Fe$^{\text{III}}$, Al$^{\text{III}}$). However, previous studies have not indicated the formation of hydroxy-species with univalent metal ions such as thallium(I).

The use of ^{13}C n.m.r. clearly demonstrates the formation of $[\text{M}(\text{cdtn})\text{X}]^{n-}$ species as shown by our studies of $[\text{Co}^{\text{III}}(\text{cdtaH})\text{Cl}]^-$ (formed from $[\text{Co}(\text{cdta})]^-$ in conc. HCl)[3] and, more unexpectedly, $[\text{Tl}^{\text{I}}(\text{cdta})\text{OH}]^{4-}$. The latter species is revealed from a study of $[\text{Tl}(\text{cdta})]^{3-}$ at 270 K and above pH 12. The ^{13}C chemical shifts, which are substantially different from those of the free ligand, are given in the table.

The assignments are made on the basis of predicted shifts,[4] off-resonance decoupling, and of the study of some fifteen different diamagnetic $[\text{M}(\text{cdta})]^{n-}$ complexes.[5] In all of these the mean axial (out of the N–M–N plane) glycinate methylene carbon shifts are 3·5 to 8 p.p.m. upfield from the mean equatorial (in the N–M–N plane) glycinate CH_2 carbon shifts, almost certainly because of their steric crowding by cyclohexyl ring protons. Clear identification of the axial glycinate carbon resonances has also come from a study[5] of the effect of selective deuteriation[6] at the axial glycinate CH_2 groups in $[\text{Co}(\text{cdta})]^-$ and $[\text{Co}(\text{cdtaH})\text{Cl}]^-$. It may be noted that, as with the complexes of the ethylenediaminetetra-acetate ion (edta), the Co$^{\text{III}}$ shifts are generally upfield from those of other complexed metal ions, probably because of temperature independent paramagnetism.

The thallium(I) spectra obtained at pH 13 and 270 K show sufficient resolved peaks to rule out the presence of octahedral $[\mathrm{Tl(cdta)}]^{3-}$, but are fully consistent with the shifts expected for $[\mathrm{Tl(cdta)OH}]^{4-}$. In particular the unsymmetrical splitting of the axial $\mathrm{CH_2}$-peak between pH 9·6 and 13 suggests that one axial glycinate ligand has been replaced by another species, presumably $\mathrm{OH^-}$. Polymerisation is unlikely since the shifts are unaffected by dilution of the complex. At pH 9·6 cdta is probably acting as a sexidentate ligand, although pseudo-C_2 symmetry on the n.m.r. timescale could also be achieved by rapid interconversion between $[\mathrm{Tl^I(cdta)OH}]^{4-}$ and $[\mathrm{Tl^I(cdta)}]^{3-}$, even if the former species still predominated.

TABLE

^{13}C Chemical shifts (p.p.m. relative to $\mathrm{Me_4Si}$) of cdta complexes of cobalt(III) and thallium(I)

Complex	pH	Temp./K	$\mathrm{CO_2^-}$	Ring CH	Equatorial glycinate $\mathrm{CH_2}$	Axial glycinate $\mathrm{CH_2}$	Ring $\mathrm{CH_2}$
$\mathrm{K_4cdta}$	>12	303	181·2	61·7	56·1[a]		26·8, 24·5
$[\mathrm{Co(cdta)}]^-$	8	303	183·7 (×2)[b] 183·1 (×2)[c]	73·3	65·1	59·3	26·8, 23·8
$[\mathrm{Co(cdtaH)Cl}]^-$ [d] . .	(conc. HCl)	303	185·4[b], 185·2[b] 184·3[c], 168·3[e]	75·4 74·0	65·6 61·7[e]	59·8 59·3	28·3, 27·4 24·9, 24·3
$[\mathrm{Tl(cdta)}]^{3-}$	9·6	270	180·6 (×2)[b] 179·9 (×2)[c]	61·2 (×2)	56·2 (×2)	52·7 (×2)	26·2 (×2) 24·9 (×2)
$[\mathrm{Tl(cdta)OH}]^{4-}$ [f] . .	>12	270	180·5 (×3)[b] 179·2[c]	61·4 61·2	56·9 55·5	53·3 51·7[e]	26·2 (×2) 25·3 24·4

[a] Around pH 10 and upon cooling to lower temperatures this peak broadens then splits into 2 peaks at 57·8 and 53·2 p.p.m. The dynamics of this system will be discussed in a later publication. [b] Probably "axial." [c] Probably "equatorial." [d] Shifts corrected for an acid medium effect on the basis of the unchanged $[\mathrm{Co(cdta)}]^-$ shifts between the two media. [e] Unco-ordinated. [f] To minimise exchange a slight excess of $\mathrm{cdta^{4-}}$ is necessary; total $[\mathrm{cdta^{4-}}] = 0{\cdot}50\ \mathrm{mol\ l^{-1}}$, total $[\mathrm{Tl^I}] = 0{\cdot}475\ \mathrm{mol\ l^{-1}}$.

Confirmation of our assignment comes from selective relaxation experiments with the addition of a low concentration of a paramagnetic probe such as a manganese(II) complex. For example, when $0{\cdot}03\ \mathrm{mol\ l^{-1}}$ $[\mathrm{Mn(edta)}]^{2-}$ is added to $0{\cdot}5\ \mathrm{mol\ l^{-1}}$ $[\mathrm{Co(edta)Cl}]^{2-}$ it preferentially quenches the nuclear Overhauser enhancement of the unco-ordinated glycinate methylene carbon, presumably because of preferential interaction with the free carboxylate group. Similarly, when $[\mathrm{Mn(cdta)}]^{2-}$ is added to $[\mathrm{Tl(cdta)OH}]^{4-}$ it selectively halves the height of both of the axial glycinate methylene resonances (at $\delta = 53{\cdot}3$ and $51{\cdot}7$ p.p.m.) leaving the other two equatorial glycinate methylene resonances (at $\delta = 56{\cdot}9$ and $55{\cdot}5$ p.p.m.) largely unaffected (apart from a small amount of residual broadening which is also observed with the cyclohexane ring carbons). This confirms that the thallium(I) complex is axially substituted by hydroxide ion. The reduction in height of both of the axial $\mathrm{CH_2}$ resonances is explained by significant residual exchange of the type noted above. Although the overall exchange rate (judged from residual line broadening) indicates a lifetime of *ca.* 0·03 s for the hydroxy species, this is still sufficiently short to prevent proton polarisation being built up on one axial glycinate methylene whilst the other is unco-ordinated.

We are currently investigating selective relaxation in other penta-co-ordinate complexes of cdta and edta, and believe that the method offers considerable promise in aiding ^{13}C n.m.r. assignments.

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