Carbon-13 Nuclear Magnetic Resonance Study of Metal Complexes of Ethylenedinitrilo-*NNN'N'*-tetra-acetic Acid (H_4edta)

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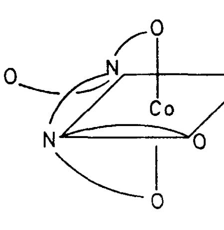
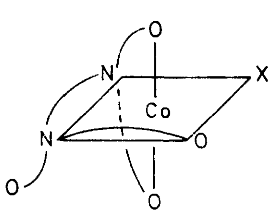
^{1}H-Decoupled ^{13}C n.m.r. spectra of Zn^{II}, Cd^{II}, Hg^{II}, Pb^{II}, Tl^{I}, Al^{III}, and Co^{III} complexes of edta^{4-} and Hedta^{3-} are reported. The results confirm and extend earlier studies of the labile complexes of Zn^{II}, Cd^{II}, Hg^{II}, and Pb^{II}, and reveal averaged hyperfine couplings between the carboxylate carbon atoms and ^{111}Cd or ^{113}Cd [^2J(C–Cd) 12·1 Hz] or ^{199}Hg [^2J(C–Hg) 35 Hz]. Aluminium(III) gives an unsymmetrical complex at high pH. Spectra of complex ions of the type $[\mathrm{Co^{III}(edta)X}]^{n-}$ or $[\mathrm{Co^{III}(Hedta)X}]^{(n-1)-}$ (X = Cl, Br, NO_2, OH, or OH_2) confirm the expected quinquedentate co-ordination of edta^{4-} and reveal that only one (' equatorially ' substituted) isomer is present, except when X = Br where two distinct isomers (' axial ' and ' equatorial ') exist. A previously reported single isomer of $[\mathrm{Co^{III}(edta)Br}]^{2-}$ is tentatively assigned an axial structure instead of the expected equatorial configuration.

ETHYLENEDINITRILO-*NNN'N'*-TETRA-ACETATE ANION (edta^{4-}) forms metal complexes of co-ordination number six with a wide variety of metal cations. Its complexes with Zn^{II}, Cd^{II}, and Hg^{II} are known from proton n.m.r. studies[1] to be labile at low pH; however, metal–nitrogen bond cleavage is slow (on the n.m.r. timescale) at higher pH. The nature of the complex formed between Al^{III} and edta is known to vary with pH,[2] but the structures of the species present in solution are unknown. Cobalt(III) is known to form not only a simple inert sexidentate complex but also a series of inert quinquedentate complexes where one co-ordination position is occupied by unidentate ligands such as Cl$^-$, Br$^-$, or H_2O, leaving one carboxylate group unco-ordinated. The structures of these quinquedentate complexes are only partially known.[3-5] There are four geometric isomers possible, (I)—(IV). Of these four structures, (II) and (IV) are less likely to form by acid-catalysed ring opening of the $[\mathrm{Co^{III}(edta)}]^-$ ion since to do so requires opening of at least two glycinate–metal rings. Conversely, chelate-ring closure is not possible in (II) or (IV) without prior opening of a further glycinate–metal ring. It is also probable that structures (II) and (IV) involve more ring strain than (I) and (III). We will follow previous practice, therefore, in provisionally discounting the possibility of isomers (II) and (IV), and also in referring to (I) as an equatorially substituted complex, and (III) as axially substituted. Since all the complexes of the type $[\mathrm{Co(edta)X}]^{n-}$ that have been synthesised so far are found to ring close readily, this hypothesis seems reasonable and our results support this conclusion in so far as they show that only one or (in one case) two isomers are present in above 5% concentration in the solutions studied. With one exception, recent studies have proposed the equatorially substituted structure (I) as being the only isomer present in quinquedentate $[\mathrm{Co^{III}(edta)X}]^{n-}$ complexes.[3,5-7] Structure (I) has been established by *X*-ray analysis for $[\mathrm{Cr^{III}(Hedta)H_2O}]$,[8] for (ethylenedinitrilo-*NNN'*-triacetato)nitrocobaltate(III),[9] for each half of the complex ion $[(\mathrm{Cu^{II}})_2(\mathrm{H_2O})_2\mathrm{L}]$, (L = 3,6-diazaoctanediamine-*NNN'N''*-*N'''N'''*-hexa-acetato),[10] and proposed on ^{1}H n.m.r. evidence for $[\mathrm{Co^{III}(edta)NO_2}]^{2-}$. Also Hoard[11] has shown from the *X*-ray structure of the $[\mathrm{Co^{III}(edta)}]^-$ ion that the equatorial carboxylate–metal–nitrogen rings (glycinate rings) are more strained than the corresponding axial rings, suggesting that they will break open

'Equatorial'

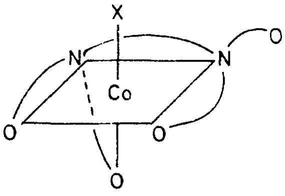


(I)

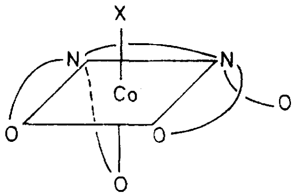


(II)

'Axial'



(III)



(IV)

In isomers (II) and (IV) the free carboxylate oxygen atom cannot bridge to position X.

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[1] (*a*) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Amer. Chem. Soc.*, 1963, **85**, 2930; (*b*) R. J. Day and C. N. Reilley, *Analyt. Chem.*, 1964, **36**, 1073; (*c*) G. H. Reed and R. J. Kula, *Inorg. Chem.*, 1971, **10**, 204.

[2] F. P. Dwyer and D. P. Mellor, ' Chelating Agents and Metal Chelates,' Academic Press, New York, 1964.

[3] M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.*, 1956, **78**, 5178; *J. Phys. Chem.*, 1959, **63**, 340.

[4] F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, 1958, **80**, 4480.

[5] R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1960, 1998.

[6] G. L. Blackmer and J. L. Sudmeier, *Inorg. Chem.*, 1971, **10**, 2019 and refs. therein; M. L. Morris, M. E. Banasik, and J. Knoeck, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 331.

[7] B. Grossman, Ph.D. Thesis, State University of New York, Buffalo, 1967.

[8] J. L. Hoard, C. H. L. Kennard, and G. S. Smith, *Inorg. Chem.*, 1963, **2**, 1316.

[9] J. D. Bell and G. L. Blackmer, *Inorg. Chem.*, 1973, **12**, 836.

[10] P. Leverett, *J.C.S. Chem. Comm.*, 1974, **5**, 161.

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

more readily in the presence of the competing ligand X^-. Furthermore, it has been shown for $[Co^{III}(edta)]^-$ that, because of the different ring strains, the CH_2 protons on the axial glycinate rings will exchange more rapidly with aqueous solvent protons under acid or alkaline conditions than do the equatorial glycinate protons.[12] Application of this information to ^1H n.m.r. spectra of $[Co^{III}(edta)NO_2]^{2-}$ in various states of deuteriation has also confirmed the equatorially substituted structure (I).[6]

The one exception to this has been in kinetic studies [3,5,7] of the ring-closure reaction of aqueous $[Co^{III}(edta)Br]^{2-}$. When the complex was prepared by the reaction (1),

$$[Co^{II}(edta)]^{2-}(aq) + Br_2 \longrightarrow 2[Co^{III}(edta)Br]^{2-}(aq) \quad (1)$$

a product was obtained which, from its non-exponential kinetics of ring closure, appeared to be a mixture of isomers. However, when the complex was prepared by a different method, (2), a single isomer was obtained.[7]

$$[Co^{III}(edta)]^-(c) + \text{conc. } HBr \longrightarrow [Co^{III}(Hedta)Br]^-(c) \quad (2)$$

Grossman [7] proposed that this was the equatorially substituted isomer, although noting that its ring-closure kinetics were those of the less-stable isomer from reaction (1). [It should be noted that if reaction (2) is attempted in the homogeneous liquid phase it merely results in reduction to Co^{II} species.]

EXPERIMENTAL

Reagents used were the best commercially available materials.

Synthesis of Complexes.—These were prepared by standard methods, the references to which are given in the Table, and identified by their visible spectra. Acid-catalysed deuteriation [12] of $[Co^{III}(edta)]^-$ was carried out at 371 K in 0·5 mol l^{-1} HNO_3 in D_2O, the extent of deuteriation being checked by proton n.m.r. spectroscopy; 17·5 h were necessary for complete deuteriation of the axial glycinate carbons, and 170 h for total deuteriation of the glycinate carbon atoms. The ethylenic protons were totally inert. The resulting $K[Co^{III}\{(^2H_4)edta\}]$ and $K[Co^{III}\{(^2H_8)edta\}]$ were used to prepare other selectively deuteriated quinquedentate Co^{III} complexes as an aid to assignment of their ^{13}C n.m.r. spectra.

Solutions were made up to between 0·3 and 1 mol l^{-1} in 10—100% D_2O–H_2O as appropriate, and were examined at either room temperature or 280 K. (The temperature coefficients of the chemical shifts in neutral solution were *ca.* +0·027 p.p.m. K^{-1}.) Labile complexes were basified dropwise with stirring (monitored with a pH meter). Solid complexes of the type $[Co^{III}(Hedta)X]^{(n-1)-}$ were basified with Na_2CO_3 to obtain the more soluble ions $[Co^{III}(edta)X]^{n-}$. The two $Hedta^{3-}$ complexes studied ($X = Cl$ and H_2O) were prepared directly by adding $[Co^{III}(edta)]^-$ respectively to conc. HCl and conc. $HClO_4$ (or HBF_4), and were not isolated. The reactions in conc. HCl showed no trace of starting material after 10 min. However, even when equilibrium had been obtained (30 min), *ca.* 30% of the aqua-complex was present in solution together with the chloro-complex. The reaction in $HClO_4$ gave *ca.* 50% conversion in 2M-acid, through to 90% conversion in 8M-acid.*

Summary of observed ^{13}C n.m.r. shifts (p.p.m. from Me_4Si) of edta and its metal complexes

			CO_2^-			CH_2			
Compound	Preparation ref.	T/K	Equatorial	Axial	Unco-ordinated	Equatorial	Axial	Unco-ordinated	Ethylenic
$[Co^{III}(edta)]^-$		280	182·4	183·0		65·8	66·0		64·0
$[Co^{III}(edta)Cl]^{2-}$	*a*, 7	280	183·7	184·8, 185·3	173·4	66·9	65·2, 66·1 [b]	66·1 [b]	62·3, 64·7
$[Co^{III}(Hedta)Cl]^-$ [c]	*d*	305	183·8	184·7, 185·2	169·2	66·9	65·5, 65·8	63·8	62·3, 64·8
$[Co^{III}(edta)Br]^{2-}$, (I)	*a*	280	183·7	184·8, 185·3	173·4	66·8	65·2, 66·1 [b]	66·1 [b]	62·3, 64·7
$[Co^{III}(edta)Br]^{2-}$, (III)	*a*, 7	280	185·5 [b]	184·1 [e]	173·7	66·4, 64·5	66·8	66·4 [b]	62·0, 64·3
$[Co^{III}(edta)OH]^{2-}$	*a*	280	183·7	184·8, 185·3	173·9	66·9	66·5, 655 [b]	65·5 [b]	61·5, 64·5
$[Co^{III}(Hedta)H_2O]$ [f]	*d*	280	182·6	183·8, 184·3	169·6	67·4	66·4, 64·7	62·6	61·8, 63·4
$[Co^{III}(edta)NO_2]^{2-}$	*a*	280	182·7	185·9, 183·4	173·0	66·6	65·1,[b] 64·8	65·1 [b]	61·4, 64·4
$edta^{4-}$	pH 13	304	180·6 [g]			60·0 [g]			52·8
$[Tl^{I}(edta)]^{3-}$	pH 10·3	323	180·4 [g]			59·7 [g]			53·6
$[Pb^{III}(edta)]^{2-}$	pH 6	304	180·0 [g]			59·3 [g]			54·2
$[Zn^{II}(edta)]^{2-}$	pH 6	304	179·9 [g]			62·7 [g]			57·9
$[Cd^{II}(edta)]^{2-}$	pH 9	304	179·4 [g]			59·6 [g]			54·8
$[Hg^{II}(edta)]^{2-}$	pH 9·0	305	177·4 [g]			59·2 [g]			52·0
$[Al^{III}(edta)OH]^{2-}$	pH 9·6	275	178·1, 177·8, 176·9			63·4, 61·2, 60·5			56·0

[a] G. Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839. [b] Superimposed peaks: typical linewidth 0·2 p.p.m. for CH_2, 0·1 p.p.m. for CO_2 groups. [c] Shifts corrected for acid medium effects by analogy with aqua-complex. The actual shifts observed were 185·0, 185·9, 186·4, 169·6, 67·6, 66·5, 66·2, 65·6, 63·7, and 63·0 p.p.m. [d] See Experimental section. [e] In the mixture of isomers this resonance was at δ 184·2 p.p.m. Because of typographical error this is printed in ref. 16 as 182·2 p.p.m. [f] Shifts as in 2M-$HClO_4$, to eliminate acid medium effect. [g] Rapid exchange of in-plane and out-of-plane sites.

Measurements.—22·628 MHz ^{13}C Fourier-transform spectra were measured on a Bruker WH90 spectrometer with noise-modulated ^1H decoupling. Chemical shifts were calibrated with respect to external (capillary) Me_4Si. Between 1 000 and 10 000 fast scans were accumulated for each spectrum, after locking on to the solvent deuterium resonance.

RESULTS AND DISCUSSION

Our results are summarised in the Table.

$K_4[edta]$.—The potassium salt was investigated, since complexing with sodium ions is significant.[13] The pH

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* 1M = 1 mol dm^{-3}.

[12] J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *Inorg. Chem.*, 1971, **10**, 90.

[13] T. L. James and J. D. Noggle, *J. Amer. Chem. Soc.*, 1969, **91**, 3424.

variation of the carboxylate part of the ^{13}C n.m.r. spectrum was checked and found to agree with previous measurements.[14] The resonances of the glycinate and ethylenic carbon atoms were each found to vary by less than 1·3 p.p.m. between pH 4·7 (H_2edta^{2-}) and 13 ($edta^{4-}$). This observation may be compared with upfield carboxylate and methylene shifts of 3—4 p.p.m. on protonation of the unco-ordinated glycinate group in $[Co^{III}(edta)Cl]^{2-}$ (see below) and thus provides further evidence for the *N*-protonation of free $edta^{4-}$.

$[M^{II}(edta)]^{2-}$ (M = Zn, Cd, Hg, *or* Pb) *and* $[Tl^{I}(edta)]^{3-}$.—Only one carboxylate and one glycinate peak could be distinguished up to the maximum attainable pH (6—10) for all these complexes. However, this is almost certainly due to rapid interchange of carboxylate groups between axial and equatorial positions, rather than to total exchange of (edta), because in $[Cd^{II}(edta)]^{2-}$ and $[Hg^{II}(edta)]^{2-}$ we were able to detect averaged hyperfine couplings between the metal and the carboxylate carbon atoms. The coupling constants were: ^{2}J(Cd–C) (average between axial and equatorial CO_2^-, and between ^{111}Cd and ^{113}Cd) 12·1; ^{2}J(Hg–C) (average between axial and equatorial CO_2^-, and ^{199}Hg) 35 Hz. These are closely comparable in magnitude to metal–proton couplings observed by Day and Reilley.[1b] The Cd–C coupling was also reported by Roberts and his co-workers,[14] but they were unable to resolve the Hg–C coupling. We were not able to resolve any couplings between the metal ions and any of the CH_2 carbons, however, despite the fact that these would also be ^{2}J couplings. Also we could not detect any couplings to ^{205}Tl or ^{203}Tl. Our carboxylate carbon chemical shifts agreed quite closely with those listed by Roberts and his co-workers. A similar, strikingly small, shift variation was apparent for both the glycinate and ethylenic carbon atoms; this is consistent with the pH insensitivity of these resonances in the free ligand. It is presumably also due to near-cancellation of diamagnetic and paramagnetic contributions from the co-ordinated metal ion. (In confirmation of this we note that the shifts for Al^{III} showed that charge on the metal atom is not of major importance in determining chemical shifts.)

$[Al^{III}(edta)]^-$.—Possible structures proposed for this complex include a symmetrical sexidentate ion, a quinquedentate ion in which the sixth ligand is H_2O, OH^-, or bridging oxygen, and possibly also quadridentate species.[15] Our own measurements showed both pH and temperature dependence, and are summarised in Figure 1. At high pH the complex is clearly not sexidentate (or symmetrically quadridentate). However, even by reducing exchange as far as possible by careful addition of alkali and by cooling to 271 K, we were unable to resolve separate peaks for each of the ten resonances expected for an unsymmetrical complex ion. This indicates either unusual chemical-shift coincidences or partial lability of a quinquedentate complex, with the axial sites remaining distinct from the equatorial. The second interpretation would require the two axial glycinate, and also the two ethylenic CH_2, chemical shifts in the absence of exchange to be closer to each other than those of the equatorial and free glycinate CH_2 groups. At pH *ca.* 8 the spectra at both temperatures showed that the complex has C_2 symmetry on the ^{13}C n.m.r. timescale. Two interpretations of this are reasonable. Either the complex becomes sexidentate, or it remains quinquedentate but undergoes more rapid exchange of the type described above. At low pH a three-line spectrum was observed, as expected for a more labile complex.

$[Co^{III}(edta)]^-$.—The chemical shifts for this complex, and even more so for its derivatives, were all of the order of 5 p.p.m. downfield from those in the corresponding aluminium, zinc, cadmium, thallium, and lead complexes. This may be explained by the greater temperature-independent paramagnetic (t.i.p.) contribution of the Co^{III} ion. The presence of three methylene and two carboxylate resonances in our spectra is entirely consistent with the known inert sexidentate structure. When the complex was deuteriated at the axial glycinate methylene carbon atoms, the downfield carboxylate peak (δ 183·4 p.p.m.) and the downfield methylene peak (δ 66·2 p.p.m.) were greatly reduced in height, and also slightly broadened. This is due to removal of the proton nuclear-Overhauser enhancement, and to unresolved C–D hyperfine splittings. This observation establishes that these resonances belong to the axial glycinate ligands, and also further demonstrates the inertness of the complex. Further deuteriation of the equatorial glycinate methylene carbon atoms left only the peak at δ 64·2 p.p.m., which we therefore assign to the ethylenic carbon atoms.

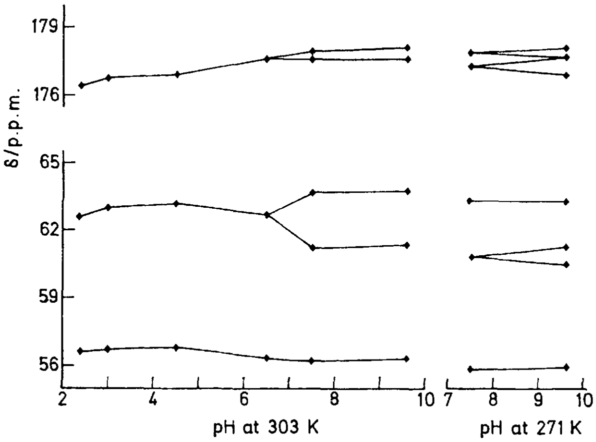

FIGURE 1 pH and Temperature dependence of ^{13}C n.m.r. spectra of the $[Al^{III}(edta)]^-$ complex

$[Co^{III}(edta)Cl]^{2-}$ *and* $[Co^{III}(Hedta)Cl]^-$.—The mean chemical shift of the bound carboxylate carbon atoms in these complex ions was 1·5 p.p.m. further downfield

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

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

from that in [Co^{III}(edta)]$^-$. A similar observation holds for all the other quinquedentate complex ions studied. This may indicate a larger t.i.p. contribution from the metal atom, which would be consistent with the move of the first visible-absorption maximum to longer wavelength (from 18 600 to 17 100 cm^{-1}). The presence of ten peaks is consistent with the expected quinquedentate structure. The identification is as follows. (*i*) The free carboxylate peak [δ(alkaline) 173·4 p.p.m.] was clearly identified by its unique position and also by its uniquely large pH dependence [δ(acid) 169·2 p.p.m. at pH <0]. (*ii*) The free glycinate ligand [δ(alkaline) 66·1 p.p.m.] was also identified by its uniquely large pH dependence [δ(acid) 63·8 p.p.m. at pH <0]. (*iii*) Axial glycinate methylene and carboxylate carbon atoms were identified by preparation of the complex from ([$^2H_4$]axial)[Co^{III}(edta)]$^-$. The observation that the four resonances affected by deuteriation differed from the CH_2 and CO_2 free-glycinate resonances confirms the previously unproven supposition that the chloro-complex is equatorially substituted, almost certainly having structure (I). (*iv*) Ethylenic carbon resonances were identified by repeating the preparation starting with [Co^{III}{($^2H_8$)edta}]$^-$. Whilst it is not surprising to find these resonances upfield from those of the glycinate carbon atoms, it is surprising to find such a large chemical shift (2·4 p.p.m.) between them. This pattern was repeated in all the five-co-ordinate cobalt(III)-edta complexes, although not apparently in the corresponding aluminium complex, and is discussed later.

All the resonances of [Co^{III}(Hedta)Cl]$^-$, except those of the free-glycinate arm, differed by less than 0·3 p.p.m. from those of [Co^{III}(edta)Cl]$^{2-}$, after a solvent correction had been applied (derived from data for [Co^{III}(Hedta)-H_2O] in various solvents). However, the free CH_2 resonance moved to δ 63·8 p.p.m. and the free CO_2H resonance to δ 169·2 p.p.m. This is all further confirmation that protonation in strong acid is exclusively at the free carboxylate, and that the overall charge of the complex ion is not important in determining ^{13}C chemical shifts of the edta^{4-} ligand.

[Co^{III}(edta)Br]$^{2-}$.—Our measurements on this complex have been reported in a preliminary communication.[16] Unfortunately we were not able to prepare the corresponding Hedta^{3-} complex in sufficient concentration to obtain a spectrum, so that we were not able to identify the free-glycinate CH_2 resonances for the bromo-complex. When the bromo-complex was prepared by bromine oxidation of [Co^{II}(edta)]$^{2-}$, the ^{13}C n.m.r. spectrum clearly indicated the presence of a *ca.* 2 : 1 mixture of isomers (Figure 2). The minor component had chemical shifts which were remarkably close to those found for the chloro-complex. We next investigated the reported single isomer prepared in the solid state [reaction (2)].[7] Although this isomer is the faster to ring close of the two isomers prepared by the former route [reaction (1)], Grossman assigned structure (I) to it and (III) to the other isomer. However, the ^{13}C n.m.r. spectrum of the single isomer fitted precisely with that of the major isomer in the spectrum of the mixture, leaving no peak unexplained. We therefore assign structure (I) to the minor isomer and (III) to the major one [bearing in mind that structures (II) and (IV) are not unequivocally eliminated by our results]. Our reassignment explains why the more common isomer ring closes more rapidly than the less common one: axial glycinate rings are generally less strained than equatorial ones. We can reasonably identify the separate resonances in the equatorial isomer by analogy with the isostructural chloro-complex. The coincidence of chemical shifts was too close to permit any ambiguity. We also identified the ethylenic resonances of both isomers as being the furthest upfield, by the use of [$^2H_8$]edta^{4-} in the preparation of the isomer mixture. The attempt to identify the axial-glycinate resonances in the axially substituted isomer by starting with [Co^{III}{($^2H_4$)edta}]$^-$ was somewhat less successful. The two upfield carboxylate resonances were reduced in intensity by *ca.* 30%, which confirms the assignment of structure (III) rather than (II) but is only just outside the experimental error. The unreduced methylene peaks are almost certainly those at δ 66·4 (one) and 64·5 p.p.m., although the spectrum was not well resolved because of ^2H broadening. This assignment would leave the free methylene as the other δ 66·4 p.p.m. peak (by analogy with other free methylenes) and the bound axial methylene at δ 66·8 p.p.m.

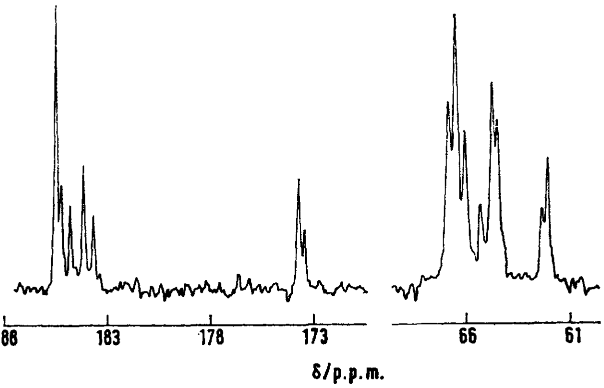

FIGURE 2 ^1H-Decoupled ^{13}C n.m.r. spectrum of the isomer mixture of [Co^{III}(edta)Br]$^{2-}$

[Co^{III}(edta)OH]$^{2-}$.—This ion is known to be relatively unstable in alkaline aqueous solution. We obtained an n.m.r. spectrum whose chemical shifts (particularly in the carboxylate region) were close to those for [Co^{III}-(edta)Cl]$^{2-}$. We therefore propose that [Co^{III}(edta)-OH]$^{2-}$ also has structure (I), with its resonances assigned as for [Co^{III}(edta)Cl]$^{2-}$. The spectrum broadened noticeably after *ca.* 15 min at 275 K, indicating the onset of reduction to a cobalt(II) complex.

[Co^{III}(edta)NO_2]$^{2-}$.—The assignment of this spectrum presented some difficulties. The ethylenic carbon atoms were easily identified as before. But once again the

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

complex was not sufficiently soluble in acid solution to permit easy identification of the unco-ordinated CH_2 group. However, its resonance fortunately identified itself by a small (0·5 p.p.m.) variation with pH in the available alkaline range (*ca.* pH 4—11). The [$^2H_4$] complex gave a somewhat broadened spectrum in which only the multiple peak at *ca.* 65·0 p.p.m. was definitely lowered in intensity. This evidence gives a methylene assignment consistent with the other complexes, with the single bound in-plane ligand having the largest shift. Further evidence for this assignment came from a spectrum obtained without ^1H decoupling from the [$^2H_2$] complex (deuteriation only at the bound axial methylene).[6] In the carboxylate region the δ 182·7 and 185·9 p.p.m. peaks showed 1 : 1 : 1 : 1 quartet hyperfine coupling from the α-CH_2 group, as expected for a bound ligand. The δ 173·0 p.p.m. peak showed 1 : 2 : 1 triplet splitting; this can be attributed to free rotation about the H_2C–CO bond averaging the ^2J(C–H) coupling constants. However, the δ 183·4 p.p.m. peak was smaller and narrower, which is what would be expected for ^2J(C–D) splitting. We therefore assign this peak to the bound axial carboxylate furthest from the free-glycinate arm. The methylene region gave a more complicated, broader, spectrum, because of the more complex ^3J(C–H) splittings. However, all the resolved resonances showed 1 : 2 : 1 (or 1 : 1 : 1 : 1) splitting. This shows that the single resonances all come from CH_2 groups, and therefore confirms that the deuteriated methylene resonance lies under the other resonances at δ 65·0 p.p.m. Also the δ 66·6 p.p.m. resonance was noticeably less broad than the others, consistent with its being due to the in-plane methylene nearest to the deuteriated out-of-plane methylene group. Both these items of information confirm the proposed structure (I).[17] ^1J(C–H) Coupling constants were also obtained from the decoupled spectrum. Those of the ethylenic and bound equatorial-glycinate methylene carbon atoms were **145** Hz, whereas the average coupling constant of the axial- and (neighbouring) unco-ordinated-glycinate methylene carbon atoms was 142 Hz. For chemically similar carbon atoms, the magnitude of ^1J(C–H) is known to correlate with angle strain at that carbon.[18] Our results therefore confirm Hoard's contention [11] that the equatorial chelate ring is more strained than the axial one.

[Co^{III}(Hedta)H_2O].—This complex, although uncharged, was nevertheless highly soluble in all the aqueous solvents used. It was obtained by dissolving K[Co^{III}(edta)] in strong acid; spectra were obtained using 8, 4, and 2 mol l^{-1} $HClO_4$, 4·2 mol l^{-1} HBF_4, and (as a by-product) 8·2 mol l^{-1} HCl. The n.m.r. peaks showed small solvent shifts between 2 and 4 mol l^{-1}, and rather larger ones in 8 mol l^{-1} acid. The bound-carboxylate solvent shifts were *ca.* +1·2 p.p.m. in both 8 mol l^{-1} $HClO_4$ and 8 mol l^{-1} HCl, and the bound-methylene shifts *ca.* +0·3 p.p.m. for 8 mol l^{-1} $HClO_4$, and +0·7 p.p.m. for 8 mol l^{-1} HCl. As the protonation shifts of the free-carboxylate ligand were in the reverse direction, the solvent shifts cannot be simply attributed to further protonation. There was no great difference between the shifts in 4 mol l^{-1} $HClO_4$ and in 4 mol l^{-1} HBF_4, which confirms that perchlorate ion is not involved in complexing. The assignment of the methylene resonances was made by the usual methods. That of the carboxylate resonances is less certain because the decrease in size of the δ 183·8 and 184·3 p.p.m. resonances was small. However, the assignment is consistent with the other assignments, which place the in-plane bound carboxylate at the highest field. Our observation that the unco-ordinated ligand was not deuteriated in the [$^2H_4$] complex confirms that the ion has structure (I).

General Trends in the Chemical Shifts.—The mean chemical shift of the bound-carboxylate ligands correlated linearly with the known frequency of the first absorption maximum in the optical spectra of the complexes (Figure 3). The correlation and negative gradient of the line is consistent with the proposed changes in the t.i.p. contribution; a lower-frequency absorption should give rise to a bigger paramagnetic contribution and thus to a downfield (+δ) shift. The same principle should apply to the bound-methylene chemical shifts. The correlation was indeed similar, except for [Co^{III}(edta)]$^-$ itself which has a mean shift 1·3 p.p.m. too large. The discrepancy may be due to the different, more strained, geometry. A general feature of the equatorially substituted complexes is that the bound in-plane methylene resonance was furthest downfield. This trend was reversed in the unsubstituted and axially substituted complexes. As above, the downfield shift may be due to this ligand being the most strained. The two ethylenic carbon resonances were in both cases surprisingly well separated in the substituted complexes. As it seems unlikely that there is much variation in strain along the ethylenic chelate ring, we attribute the upfield shift {from

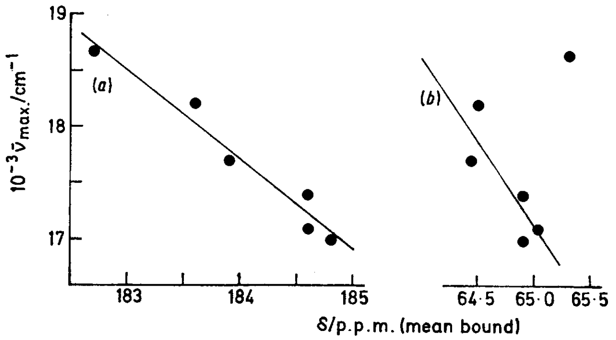

FIGURE 3 Dependence of mean chemical shift of co-ordinated CO_2 (*a*) and CH_2 (*b*) carbon atoms in cobalt(III)–edta complexes on the lowest optical-absorption maximum

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[17] G. L. Blackmer, R. E. Hamm, and J. I. Legg, *J. Amer. Chem. Soc.*, 1969, **91**, 6632.

[18] D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, 1967, **89**, 6612; D. M. Grant and B. V. Cheyney, *ibid.*, p. 5315.

$[Co^{III}(edta)]^-\}$ as due to slight steric compression of the ethylenic protons by the free-carboxylate arm.

Conclusions.—Our study was originally undertaken in order to explore the applications of ^{13}C n.m.r. spectroscopy to metal complexes. Complexes were chosen because of their known variety and because they serve to some extent as polypeptide analogues. The general conclusion from our work is that the co-ordination of polypeptides to ions of biological importance is, unfortunately, unlikely to reveal itself unequivocally in the ^{13}C n.m.r. spectra because of near-cancellation of diamagnetic and paramagnetic terms from the co-ordinated metal ion. However, our results should provide a basis for further exploration of the co-ordination chemistry of $edta^{4-}$ and related ligands. An investigation using the analogous *trans*-1,2-dinitrilocyclohexane-*NNN′N′*-tetra-acetate and 1,2-dinitrilopropane-*NNN′N′*-tetra-acetate ions is currently nearing completion.

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