Nuclear Magnetic Resonance Studies of Transition-metal Complexes of Ethylenediamine-*NNN'N'*-tetramethylphosphonate in Aqueous Solution

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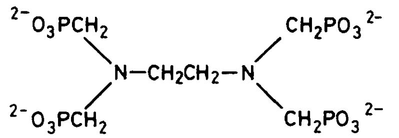
Nuclear magnetic resonance studies have been carried out on the structures of ethylenediamine-*NNN'N'*-tetramethylphosphonate (edtmp) complexes of Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Mn^{2+} in aqueous solution. It is demonstrated that the hydration numbers in these complexes are higher than for the corresponding carboxylate complexes, approximating to 1 for complexes with Cu^{2+} or Fe^{3+} and between 1 and 2 for the other complexes. Evidently, replacement of carboxyl groups by binegative phosphonate groups produces additional strain within the complex arising from increased charge repulsions and this increases the tendency to have unco-ordinated ligand groups. As expected, this effect is less important for trivalent Fe^{3+} as both its ethylenediamine-*NNN'N'*-tetra-acetate (edta) and edtmp complexes contain one water molecule in their first co-ordination spheres. Although the water molecule is replaced by a hydroxyl group above pH 7 for the edta complex of Fe^{3+}, this did not occur for the corresponding edtmp complex.

In an earlier investigation,[1] the structures of ethylenediamine-*NNN'N'*-tetra-acetate (edta) complexes of ions of the first transition series in aqueous solution were elucidated using n.m.r. relaxation studies. In this work, these studies are extended to include complexes of a structural analogue of edta, in which phosphonate groups replace carboxyl groups. Much interest has been generated in the use of phosphonate ligands ever since they were first reported[2] in 1949 and a whole new class of chelating ligands containing amino-phosphonate groups has surfaced.[3] Several reports have appeared in the literature but these have been largely concerned[4–7] with the stability of metal complexes and few investigations have dealt with their structure in aqueous solution.

Some understanding has emerged in relating the structures of this interesting group of molecules to their properties. For example, the stability constants of complexes have been explained[3] largely in terms of the charge on the phosphonate groups rather than their bulkiness. Ligands having a single phosphonate group have been shown to have a higher affinity for metal ions than the corresponding carboxylate analogues.[2,3,7] Ligands having two or more phosphonate groups have lower co-ordinating tendencies than expected[3] and this has been attributed to mutual repulsion between binegative phosphonate groups. However, such ligands may be specially effective[3] for ions having a charge greater than +2 which neutralise charge–charge repulsions and produce a higher stability for the resulting chelate compound. Mutual charge repulsions between phosphonate groups may also increase the tendency to have unco-ordinated ligand groups compared with the corresponding carboxylate analogues.[1] The aim of the present investigation was to determine the extent of water binding to edtmp complexes of transition metals in order to gain some insight into factors affecting the stereochemistry of the complexes.



Ethylenediamine-*NNN'N'*-tetramethylphosphonate (edtmp)

Experimental

The compound edtmp was obtained from Monsanto and was repeatedly recrystallised from aqueous ethanol prior to use. Solutions of edtmp containing $MnSO_4$, $CuSO_4$, $CoCl_2$, and $FeCl_3$ (all Hopkin and Williams AnalaR grade) were prepared using deionised and doubly distilled water from alkaline permanganate. Nuclear magnetic resonance measurements were made on samples in sealed glass tubes (un-degassed) as soon as possible after preparation; usually within 48 h. The edtmp to metal ion mole ratio used in the majority of experiments was 2 : 1. The pH was determined using a Radiometer pHM 84 pH meter.

N.M.R. Measurements.—The T_1 (spin-lattice) and T_2 (spin-spin) relaxation time measurements were carried out using a Bruker 322S pulse n.m.r. spectrometer operating mainly at 60 MHz. The temperature of the sample was held at 293 K and controlled to within 1 K by means of a nitrogen gas flow-temperature control system provided with the instrument. Measurement of T_1 was determined by means of a 180–τ–90° pulse program in which the n.m.r. free induction signal following the 90° pulse was obtained as a function of the pulse separation, τ; T_2 was measured using the conventional 90–τ–180° Carr–Purcell pulse sequence employing the Gill–Meiboom modification, where the separation, τ, between 180° pulses was usually set at 200 μs or 1 ms.

In the majority of cases relaxation decays and recovery curves were single exponential and T_1 and T_2 times were calculated by means of semi-log plots of signal intensity *versus* time.

Results

The relaxation times for edtmp complexes of Cu^{2+}, Ni^{2+}, and Fe^{3+} as a function of pH are shown in Figure 1. The relaxation times in solutions of transition metal ions[1] increase upon complex formation and when complexation is complete at pH 4, remain constant (Figure 1) thereafter up to pH 10—11. Potentiometric studies indicate that not all the phosphonate groups are de-protonated until pH's around 9—10 are

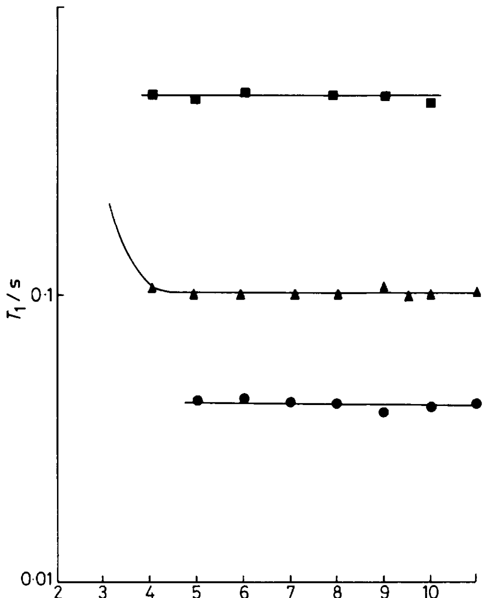


Figure 1. Plot of water proton relaxation time T_1 at 293 K and 60 MHz as a function of pH for Cu^{2+} (■), Fe^{3+} (▲), and Ni^{2+} (●) complexes of edtmp (T_2 data are omitted for convenience since $T_1 = T_2$). At pH <4, the iron(III) edtmp complex precipitates and relaxation times increase correspondingly

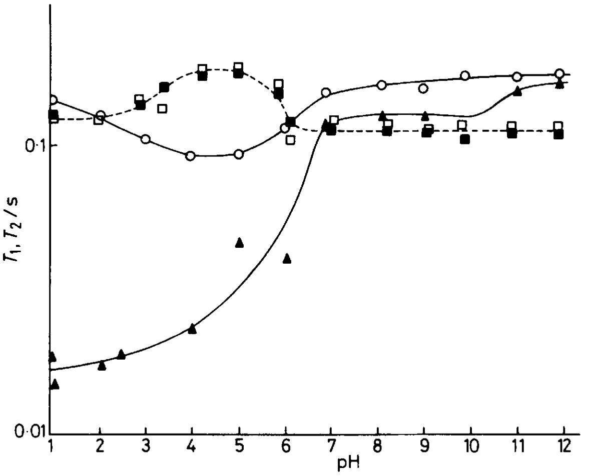


Figure 2. Plots of water proton relaxation times T_1, T_2 at 293 K and 60 MHz as a function of pH for Mn^{2+} (○, T_1; ▲, T_2) and Co^{2+} (□, T_1; ■, T_2) complexes of edtmp

reached.[5] Nevertheless, inspection of molecular models indicates that protons attached to phosphonate groups are too remote from the metal ion and they are too small in number to contribute significantly to observed relaxation rates. The lack of any movement in relaxation times with pH provides experimental confirmation. Relaxation times for edtmp complexes of Mn^{2+} and Co^{2+} are shown in Figure 2. The spin-lattice relaxation times above pH 7 are similar[1] to those of the single ions at low pH, whilst the spin-spin relaxation for the manganese complex increases upon complexation until it becomes similar to T_1. Both sets of data indicate that partial complexation occurs above pH 3 but that complexation, involving multi co-ordination by the ligand, is not complete until pH 7. Evidently, maximum co-ordination by phosphonate groups occurs only when extensive deprotonation has taken place.

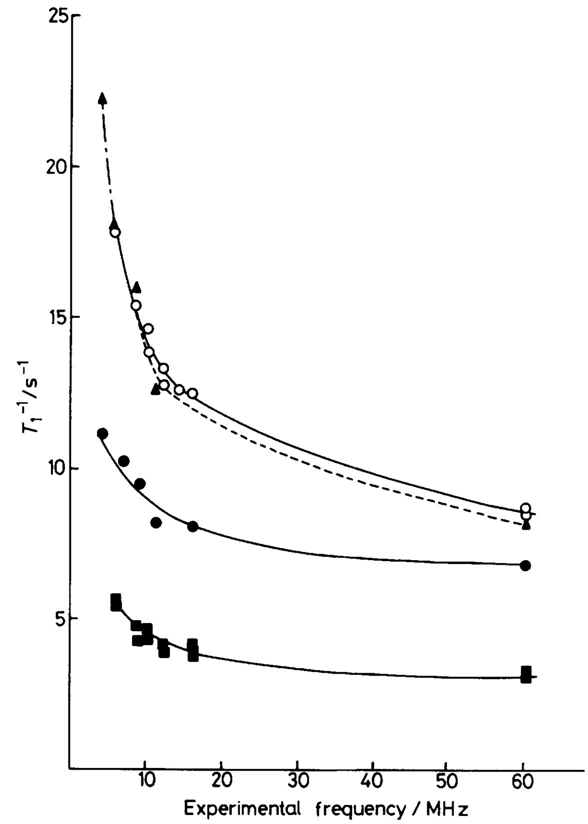


Figure 3. Variation of water proton spin-lattice relaxation rate, T_1^{-1}, with frequency for solutions containing Mn^{2+} (▲) and Cu^{2+} (○) or their respective complexes with edtmp (● and ■)

The frequency dependences of relaxation rates in solutions of Cu^{2+} or Mn^{2+} and their corresponding edtmp complexes are shown in Figure 3. After taking into account secondary solvation contributions, values of the rotational correlation time τ_r can be obtained by comparisons of relaxation rates at several different pairs of frequencies.[8] This produces the following values of τ_r for Cu^{2+}, the edtmp complex of Cu^{2+}, Mn^{2+} and the edtmp complex of Mn^{2+} of 3.6×10^{-11}, 5.5×10^{-11}, 3×10^{-11}, and 8.3×10^{-11} s respectively. The relatively high value of τ_r for the $[Mn(edtmp)]^{6-}$ complex (similar to that for the bulky $(^-O_2CCH_2)_2N[CH_2]_2O[CH_2]_2O[CH_2]_2N(CH_2CO_2^-)_2$, egta, complex[8]) may suggest incomplete co-ordination by the ligand. Interaction of one or two phosphonate groups with the solvent may hinder the re-orientational processes undertaken by the complex, leading to a longer τ_r. In keeping with previous studies of complexation by edta,[8] the electron spin relaxation time τ_s for Mn^{2+} was found to decrease upon complexation by edtmp from 1.5×10^{-8} to 1.67×10^{-9} s at 60 MHz.

Molar relaxation rates have been calculated for edtmp complexes at pH 9 and the results are given in Table 1. A detailed analysis outlined previously[1] has been undertaken using these values, which has culminated in determination of hydration numbers for the complexes, given in Table 2. Hydration numbers, n, were determined using equation (1),

$$n = [R_1]_p r^6 [\mu^2 f_1(\tau)]^{-1} n' \qquad (1)$$

where $[R_1]_p$ denotes the molar relaxation rate from primary hydration sphere water relative to a standard sample and

Table 1. Relaxation data for edtmp complexes at pH 9

Complex	Concentration/ mol dm^{-3}	T_1^{-1}/s^{-1}	$[T_1]_p^{-1}$/s^{-1}	$[R_1]_p$/s^{-1}
$[Mn^{II}(edtmp)]^{6-}$	1×10^{-3}	6.25	4.25	4.25×10^3
$[Cu^{II}(edtmp)]^{6-}$	6×10^{-3}	2.04	0.82	1.37×10^2
$[Co^{II}(edtmp)]^{6-}$	5×10^{-2}	8.33	4.76	9.5×10^1
$[Fe^{III}(edtmp)]^{5-}$	6×10^{-3}	10	6.7	1.1×10^3
$[Ni^{II}(edtmp)]^{6-}$	1×10^{-1}	25	17.31	17.31×10^1
$[Co^{II}(edtmp)]^{6-}$ + 4 × 10^{-2} mol dm^{-3} Ca^{2+}	2×10^{-2}	1	0.7	3.5×10^1

Table 2. Calculations of hydration numbers

Complex	Standard	$[R_1]_p$	μ^2	r^6	$f_1(\tau)$	n/n'	n'	n	n_{corr}
$[Mn^{II}(edtmp)]^{6-}$	Mn^{2+}	5.7×10^{-1}	1 [a]	1	2.77 [b]	0.21	6	1.20	1.32 [c] 1.44 [d]
$[Cu^{II}(edtmp)]^{6-}$	Cu^{2+}	1.85×10^{-1}	1	1	1.47	0.136	6	0.77	0.97 [c]
$[Co^{II}(edtmp)]^{6-}$	Co^{2+}	6.46×10^{-1}	7.7×10^{-1}	1	5.1	0.185	6	1.11	1.26 [c] 1.44 [d] 1.63 [e] 1.81 [f]
					7.3	0.113	6	0.68	0.77 [c] 0.88 [d] 1.00 [e] 1.11 [f]
$[Ni^{II}(edtmp)]^{6-}$	Ni^{2+}	2.22×10^{-1}	1	1	1.22	0.182	6	1.09	1.22 [c] 1.34 [d]
					0.87	0.255	6	1.53	1.71 [c] 1.88 [d]
$[Fe^{III}(edtmp)]^{5-}$	Fe^{3+}	0.1	1	1.32 [g]	7.2×10^{-1}	1.8×10^{-1}	6	1.08	1.21 [c]

[a] Assuming spin-only contribution to μ, excepting for Co^{2+} complexes which were experimentally determined; μ for Co–edtmp is similar to that of the edta complex.[1] [b] Ref. 1. [c] Assuming one phosphonate unbound. [d] Assuming two phosphonates unbound. [e] Assuming three phosphonates unbound. [f] Assuming four phosphonates unbound. [g] The Fe^{III}–H_2O distance (N. J. Hair and J. K. Beattie, *Inorg. Chem.*, 1977, **16**, 245) is 0.12 Å longer in $[Fe(edta)(H_2O)]^-$ (ref. 1) than in $[Fe(H_2O)_6]^{3+}$. Changes in r for other complexes are <0.05 Å and are ignored.

similarly, r, μ, and $f_1(\tau)$ give ratios of intermolecular distance, magnetic moment, and correlation function respectively. The known hydration number of the standard is denoted by n'. Further details can be found in Table 2. The major difference between the procedure here and that undertaken previously[1] is the need to compensate for secondary solvation contributions due to unbound phosphate groups.

Discussion

Stereochemistry.—The stereochemistry of complexes formed between metal ions and analogues of edta is influenced by several factors: (*a*) the size of the metal ion, (*b*) the strength of bonding, (*c*) crystal-field stabilisation energies, and (*d*) the backbone chain length between chelating groups.

The present investigations were undertaken with the object of establishing whether mutual charge repulsion between ligand groups affects the configuration of complexes. The observation of higher water co-ordination numbers for complexes of edtmp with transition metal ions (Table 2) compared[1] with edta, clearly, affirms this view. Evidently, increased repulsion between charged ligand groups increases the strain within the ligand molecule upon formation of six-co-ordinate complexes. This increases the tendency to have unco-ordinated charged ligand groups, hence the higher degree of water co-ordination. This is reinforced by the elimination of primary hydration sphere water when calcium ions are added during formation of the cobalt(II) complex of edtmp * (Table 1). Binding of calcium ions reduces the repulsion between phosphonate groups by neutralising the charge, facilitating octahedral or a less asymmetric co-ordination by edtmp as indicated by electronic absorption spectroscopy.[9,10]

Similarly, the need for calcium or magnesium ions for preparation of crystals[9,10] of edtmp complexes of Co^{2+}, Fe^{3+}, and Ni^{2+} may be explained in terms of counterbalancing this charge on phosphonate groups. The crystal structure of the cobalt complex has been elucidated[9] and discussed in terms of an octahedral complex containing sexidentate edtmp. Crystals of Co^{2+}, Fe^{3+}, and Ni^{2+} complexes[10] are isomorphous.

Complexes of Cu^{2+} *and* Fe^{3+}.—The hydration numbers determined for complexes of edtmp with Cu^{2+} and Fe^{3+} leave little doubt that the solution structures possess single water molecules in their first co-ordination spheres. Electronic spectroscopy and electron spin resonance studies[10] of glasses of the copper edtmp complex indicate that the complex has a distorted octahedral symmetry, similar to the edta complex. Specifically, e.s.r. studies detect only one spectrum[10] with $g_\perp = 2.06$, $g_\parallel = 2.28$, and $A_\parallel = 145 \times 10^{-4}$ T. In contrast, the edta complex exhibits[10] two spectra attributable[11] to five-co-ordinate edta ($g_\perp = 2.06$, $g_\parallel = 2.34$, $A_\parallel$ 145×10^{-4} T) and six-co-ordinate edta ($g_\perp = 2.06$, $g_\parallel = 2.30$, $A_\parallel = 152 \times$

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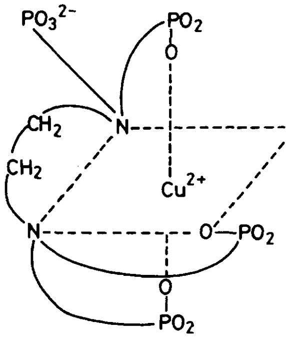
* $[R_1]_p$ for this complex is in fact smaller than that of the cobalt egta complex[1] suggesting that there may be loss of some secondary solvation water also.

10^{-4} T) in distorted octahedral environments in a 1 : 2 ratio. Whilst there is some reservation about undertaking e.s.r. studies in glasses, nevertheless there is good correspondence with the present n.m.r. studies, for both edta and edtmp complexes. Consequently, it seems likely that the dominant structure in solutions of the copper edtmp complex has an octahedral arrangement of five-co-ordinate edtmp with one water molecule completing the distorted geometry. The proposed structure for the edtmp complex of Cu^{2+} (the unco-ordinated phosphonate group is shown top left) is illustrated below.



The results for the iron(III) edtmp complex can be interpreted in terms of either a seven-co-ordinate species containing sexidentate edtmp or a six-co-ordinate species in which one phosphonate group is unbound. Electronic spectroscopy studies[9] are quite equivocal regarding the co-ordination geometry since the solvent sensitive $^6A_{1g} \longrightarrow {}^4T_{1g}$ transition lies in a position intermediate between that expected for six- or seven-co-ordination. However, the present n.m.r. results (Table 2) may tip the balance in favour of an octahedral complex containing five-co-ordinate edtmp and a water molecule in the solvation sphere. Evidence is mounting that phosphonate groups exert a lower ligand-field strength than carboxylate groups.[10] If this is correct then electronic spectroscopy results similarly are consistent with a six-co-ordinate complex.

The relaxation rate of the edtmp complex was invariant over a wide range of pH. Evidently, the pK_a for the hydrolysis reaction [equation (2)] is much higher than that recorded for

$$[Fe^{III}(edtmp)(H_2O)]^{5-} \overset{OH^-}{\rightleftharpoons} [Fe^{III}(edtmp)(OH)]^{6-} + H^+ \quad (2)$$

the corresponding edta complex. Nor is there any evidence for dimerisation or precipitation over the pH range studied. The lower pK_a for the edta complex of Fe^{3+} compared with that of Mn^{2+} is a consequence of the increased charge of the metal ion which facilitates ionisation. Similarly the failure to observe hydrolysis for $[Fe^{III}(edtmp)]^{5-}$ can be understood if the charge on the central metal ion is counterbalanced by binding of bi-negatively charged phosphonate groups or by hydrogen bonding between the bound water molecule and a neighbouring, suitably disposed phosphonate group.

Complexes of Mn^{2+}, Co^{2+}, *and* Ni^{2+}.—Hydration numbers determined for edtmp complexes of Mn^{2+}, Co^{2+}, and Ni^{2+} lie between 1 and 2. These ions have a lower charge-radius ratio than Fe^{3+} and Cu^{2+} so as expected they are less able to accommodate and retain the same number of phosphonate groups in their co-ordination spheres. These data can be analysed in terms of dynamic equilibria similar to previous edta studies[1] but between complexes containing one and two water molecules, respectively. Nevertheless, it is not attempted here until further structural information is forthcoming. Excepting the nickel complex, little is known with certainty about the stereochemistry of the complexes.

Electronic absorption studies are consistent with the nickel edtmp complex having a distorted octahedral environment similar to that obtained for crystals.[10] The symmetry of the environment of the cobalt edtmp complex is less certain whereas that for the manganese edtmp complex is unknown. The electronic absorption spectrum[9,10] of the cobalt complex is dominated by a species having a higher absorption coefficient than the corresponding edta complex suggesting a lower symmetry than octahedral but whether this is the major species still has to be determined. Studies recorded over a range of pH demonstrate that formation of the Mn^{2+} and Co^{2+} complexes is incomplete until above pH 7. Several species may co-exist in equilibrium below pH 7; the difference in relaxation times T_1 and T_2 suggest partial co-ordination of Mn^{2+} by edtmp below pH 6, multi co-ordination occurring above pH 7 when $T_1 \simeq T_2$. In view of the uncertainties expressed, it is a little premature even to attempt proposing structures for these complexes.

It has been suggested[12] that polynuclear chelate formation may occur with edtmp, although this has been disputed by others.[13] Whilst it is recognised that such structures may represent minimum energy configurations, no evidence was obtained to indicate bridging by edtmp molecules or polymerisation.

In summary, unambiguous assignment of the structures of edtmp complexes of transition-metal ions, particularly Ni^{2+}, Co^{2+}, and Mn^{2+}, is still awaited. What is clear is that edtmp complexes of the bivalent transition-metal ions have more open structures than the corresponding edta complexes which allow a greater degree of water binding to the central metal ion. Almost certainly, this is a consequence of mutual charge repulsions between binegative phosphonate groups which increases the likelihood of having unco-ordinated ligand groups. The edtmp complex of Fe^{3+} is similar to $[Fe(edta)]^-$ in containing one water molecule in the first co-ordination sphere but differs in two respects, (*i*) in overall stereochemistry and (*ii*) in that the bound water molecule does not become replaced by a hydroxyl group above pH 7.

Acknowledgements

We would like to thank Kaas von Kralingen of our Vlaardingen Laboratory for giving permission to quote details of his experiments, Diane Cummins of this laboratory for helpful discussions, Jeff Rockcliffe and Olive Laurie for the preparation and recording of samples.

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Received 5*th July* 1982; *Paper* 2/1126