Spectroscopic Studies of Transition-metal Ion Complexes of Diethylenetriaminepenta-acetic Acid and Diethylenetriaminepenta-methylphosphonic Acid

John Oakes *
Unilever Research Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW
Cornelis G. van Kralingen
Unilever Research Vlaardingen Laboratory, Olivier van Noortlaan 120, Vlaardingen, The Netherlands

The structures of diethylenetriaminepenta-acetate (dtpa) and diethylenetriaminepentamethylphosphonate (dtpmp) complexes of transition-metal ions in aqueous solution have been investigated by n.m.r., e.s.r., and electronic absorption spectroscopy. It is shown that dtpa complexes are much less hydrated than corresponding ethylenediaminetetra-acetate (edta) complexes, consistent with the increase in stability constants. The most marked reduction in water binding on replacing edta by dtpa occurs with Fe^{3+} and Mn^{2+} and it is demonstrated using e.s.r. that there is a change in overall stereochemistry from a seven- to a predominantly six-co-ordinate structure for Fe^{3+}. Other dtpa complexes adopt octahedral symmetry as do all the dtpmp complexes. Complexes of dtpmp with Co^{2+}, Ni^{2-}, and, to a lesser extent, Cu^{2+} have lower hydration numbers than the corresponding ethylenediaminetetramethylphosphonate (edtmp) counterparts, due to simultaneous binding of three nitrogen donors in dtpmp. The $[Fe^{III}(dtpmp)]^{7-}$ complex has one bound water similar to $[Fe^{III}(edtmp)]^{5-}$, but the manganese(II) complex of dtpmp is more hydrated than the corresponding edtmp complex. It is concluded that phosphonate groups produce a less effective crystal field than do carboxyl groups.

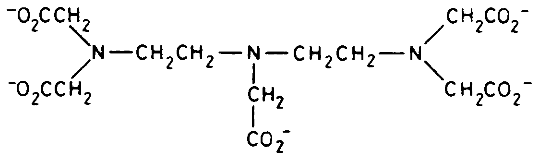
In earlier investigations [1-3] the structures of edta (ethylenediaminetetra-acetate) and edtmp (ethylenediaminetetramethylphosphonate) complexes of ions of the first transition-metal series were investigated in aqueous solution using n.m.r. spectroscopy. Here the studies are extended to include complexes of dtpa (diethylenetriaminepenta-acetate) and dtpmp (diethylenetriaminepentamethylphosphonate), higher homologues of edta and edtmp, respectively. The anion dtpa forms more stable complexes with ions of the first transition-metal series [4] than does edta which, evidently, is a consequence of the structure of the respective complexes. It has eight potential co-ordination groups and hence can form eight-co-ordinated chelated compounds, or having three nitrogen donors and five carboxyl groups has greater flexibility in forming strain-free complexes of lower co-ordination number.

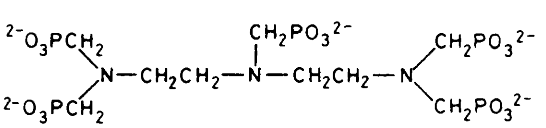
Although not all the stability constants are known for complexes of dtpmp with ions of the first transition-metal series, earlier work has demonstrated that increased mutual charge–charge repulsion between phosphonate groups is responsible for complexes of edtmp having more open structures than corresponding edta complexes.[3] Such charge repulsions can be minimised for dtpmp complexes if three nitrogens can simultaneously bind to the metal ion and, in addition, produce greater stability, since ions to the right of Mn^{2+} are known to have a stronger affinity for nitrogen atoms than oxygen atoms.[5]

Electronic absorption spectroscopy has been used to investigate the overall stereochemistry of the present complexes, together with e.s.r. spectroscopy which also provides information about the number of species present. Finally, the structures of the complexes are related to those of edta and edtmp discussed [2,3] in earlier papers.

Experimental

Sodium diethylenetriaminepenta-acetate (Na_5dtpa) was obtained as a 40% solution from BDH and diethylenetriaminepenta methylphosphonic acid (H_{10}dtpmp) either as a 50 or a 58% solution from Monsanto. Analysis of the more dilute dtpmp sample by ^{31}P n.m.r. spectroscopy showed that only 30% dtpmp was present (the more concentrated sample contained 35% dtpmp), whilst complexometric titration with Cu^{2+} indicated 50% complexing agent. The salts $MnSO_4$, $CuSO_4$, $CoCl_2$, $NiCl_2$, and $FeCl_3$ were Hopkin and Williams AnalaR grade. Complexes were formed in doubly distilled water and using a ligand to metal ratio of 2 : 1. The pH of solutions was adjusted to 9—10 where complex formation was complete. Measurements were usually made immediately after preparation or within 48 h.


dtpa


dtpmp

Details of the n.m.r. measurements have been given previously.[1,2] E.s.r. spectra at *X*-band frequency (9.1 GHz) were obtained using a Varian E-line spectrometer equipped with a 12-in magnet. Spectra of frozen solutions (0.001 mol dm^{-3}) were recorded at around 120 K. Good glasses were obtained by adding 25% (v/v) ethylene glycol to the solution. The field was calibrated using a Bruker B-NM 20 NMR apparatus. The *g* and *A* values calculated from the spectra are accurate to within 0.01 and 2×10^{-4} T, respectively. Electronic absorption spectra in the 350—1 400 nm region were recorded using a Beckman DK2 instrument and in the 290—700 nm region using a Unicam SP1800. Solutions of the corresponding zinc complexes were used as reference samples. Concentrations used were 0.02—0.04 mol dm^{-3}.

Table 1. Relaxation rates of complexes

Complex	c/mol dm^{-3}	pH	T_1^{-1}/s^{-1}	$[T_1]_p^{-1}$/s^{-1}		R_{1p}/dm^3 mol^{-1} s^{-1}	
				(*a*)	(*b*)	(*a*)	(*b*)
$[Mn^{II}(dtpa)]^{3-}$	10^{-3}	9.8	2.0	0	0.43	0	4.3×10^3
$[Mn^{II}(dtpmp)]^{8-}$	10^{-3}	9.9	7.3	5.3	5.73	5.3×10^3	5.73×10^3
$[Cu^{II}(dtpa)]^{3-}$	6×10^{-3}	8.9	1.1	−0.1	+0.15	0	2.5×10
	6×10^{-3}	9.0	1.0	−0.2	+0.05	0	9
$[Cu^{II}(dtpmp)]^{8-}$	6×10^{-3}	9.2	1.9	0.7	1.0	1.2×10^3	1.6×10^3
$[Co^{II}(dtpa)]^{3-}$	5×10^{-2}	9.0	3.1	−0.47	0.33	0	6.6
$[Co^{II}(dtpmp)]^{8-}$	5×10^{-2}	8.3	6.1	2.5	3.3	5.0×10	6.6×10
	5×10^{-2}	9.0	5.7	2.1	2.9	4.3×10	5.8×10
$[Ni^{II}(dtpa)]^{3-}$	1×10^{-1}	9.5	11.0	3.3	5.2	3.3×10	5.2×10
	1×10^{-1}	9.9	10.4	2.7	4.6	3.0×10	4.6×10
$[Ni^{II}(dtpmp)]^{8-}$	1×10^{-1}	8.0	16.2	8.5	10.4	8.5×10	10.4×10
		9.4	12.0	4.3	6.2	4.3×10	6.2×10
$[Fe^{III}(dtpa)]^{2-}$	6×10^{-3}	9.0	5.4	2.1	2.9	3.5×10^2	5.0×10^2
$[Fe^{III}(dtpmp)]^{7-}$	6×10^{-3}	9.0	10.6	7.3	8.1	1.2×10^3	1.4×10^3

[a] Assuming 2N bound in complex; $[T_1]_p^{-1}$ is the relaxation rate of primary hydration water, *i.e.* after subtracting secondary solvation contribution taken from ref. 2. [b] Assuming 3N bound in complex.

Table 2. Calculation of hydration numbers

Complex [a]	pH	$[R_1]_p$		μ^2	r^6	$f_1(\tau)$	n/n'		n		n_{corr}
		b	*c*				*b*	*c*	*b*	*c*	
$[Mn^{II}(dtpa)]^{3-}$	9.8	0	5.8×10^{-2}	1 [d]	1 [d]	1.5 [d]	0	4.0×10^{-2}	0	0.24	0.48 [e]
$[Mn^{II}(dtpmp)]^{8-}$	9.9	7.1×10^{-1}	7.8×10^{-1}	1	1	2.77	0.26	0.28	1.56	1.68	1.80
$[Cu^{II}(dtpa)]^{3-}$	8.9	0	3.4×10^{-2}	1	1	1.5	0	2.3×10^{-2}	0	0.14	0.28
	9.0	0	1.2×10^{-2}	1	1	1.5	0	8.0×10^{-3}	0	0.05	0.10
$[Cu^{II}(dtpmp)]^{8-}$	9.2	0.16	0.21	1	1	1.47	0.11	0.15	0.65	0.88	1.11
$[Co^{II}(dtpa)]^{3-}$	9.0	0	4.5×10^{-2}	7.7×10^{-1}	1	5.1	0	1.2×10^{-2}	0	0.07	0.14
	9.0	0	4.5×10^{-2}	7.7×10^{-1}	1	7.3	0	8.4×10^{-3}	0	0.05	0.10
$[Co^{II}(dtpmp)]^{8-}$	8.3	0.32	0.45	7.7×10^{-1}	1	5.1	8.7×10^{-2}	1.1×10^{-1}	0.52	0.68	0.84
	8.3	0.32	0.45	7.7×10^{-1}	1	7.3	6.1×10^{-2}	8.0×10^{-2}	0.36	0.48	0.60
	9.0	0.29	0.39	7.7×10^{-1}	1	5.1	7.4×10^{-2}	9.9×10^{-2}	0.44	0.60	0.76
	9.0	0.29	0.39	7.7×10^{-1}	1	7.3	5.2×10^{-2}	6.9×10^{-2}	0.31	0.42	0.53
$[Ni^{II}(dtpa)]^{3-}$	9.5	4.2×10^{-2}	6.7×10^{-2}	1	1	1.05	4.0×10^{-2}	6.4×10^{-2}	0.24	0.38	0.52
	9.9	3.9×10^{-2}	5.9×10^{-2}	1	1	1.05	3.7×10^{-2}	5.6×10^{-2}	0.22	0.33	0.44
$[Ni^{II}(dtpmp)]^{8-}$	8.0	1.1×10^{-1}	1.3×10^{-1}	1	1	1.05	1.0×10^{-1}	1.2×10^{-1}	0.60	0.72	0.84
	9.4	5.5×10^{-2}	8.0×10^{-2}	1	1	1.05	5.2×10^{-2}	7.6×10^{-2}	0.31	0.47	0.63
$[Fe^{III}(dtpa)]^{2-}$	9.0	3.2×10^{-2}	4.5×10^{-2}	1	1.32	8.7×10^{-1}	4.9×10^{-2}	6.8×10^{-2}	0.29	0.41	0.53
$[Fe^{III}(dtpmp)]^{7-}$	9.0	1.1×10^{-1}	1.3×10^{-1}	1	1.32	8.7×10^{-1}	1.7×10^{-1}	2.0×10^{-1}	1.0	1.18	1.36

[a] Relaxation rates and hydration numbers of standard taken from ref. 2. [b] Assuming 2N bound. [c] Assuming 3N bound. [d] Taken from earlier work for all complexes. [e] Assuming 1 $CO_2^-(PO_3^{2-})$ not bound or if 2N bound, 2 $CO_2^-(PO_3^{2-})$ not bound.

Results

(*a*) *N.M.R. Spectroscopy.*—Water proton spin–lattice relaxation rates for dtpa and dtpmp complexes of ions of the first transition-metal series at pH 9—10 are given in Table 1. Calculated molar relaxation rates for primary hydration sphere water (R_{1p}) are also given in Table 1 and, from these, water co-ordination numbers for the specified complexes can be derived (Table 2), using equation (1) where $[R_1]_p$ is the

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

molar relaxation rate of primary hydration sphere water relative to a chosen standard and r, μ, and $f_1(\tau)$ are the relative metal–water proton internuclear distance, magnetic moment, and correlation function, respectively; n' is the hydration number of the standard, taken here as the corresponding uncomplexed ion. For the ions investigated here $\mu^2 = 1$ except for cobalt where the magnetic moment has an orbital contribution which is quenched upon complexation.[2,3] Similarly, for bivalent metal ions, $r^6 = 1$ since recorded changes in internuclear distances upon complexation are exceedingly small;[1–3] for Fe^{3+}, r^6 is taken as 1.32,[2,3] since the iron–water proton distance increases by 0.12 Å upon binding of edta. (The maximum change in internuclear distance is 0.14 Å corresponding to addition of an electron to produce Fe^{2+}.) Upon complexation, additional contributions to relaxation arise from secondary solvation. As explained previously,[2,3] these have been estimated empirically using corresponding $(^-O_2CCH_2)_2N[CH_2]_2O[CH_2]_2O[CH_2]_2N(CH_2CO_2^-)_2$ (egta) complexes and subtracted from the overall relaxation. Where unbound CO_2^- or PO_3^{2-} groups are suspected a reduced secondary solvation term will apply and the calculations in Table 2 include corrections for up to two unbound groups. The correlation function $f_1(\tau)$ is dominated[2,3] by τ_r, the rotational correlation time for complexes of Cu^{2+} or Mn^{2+} and by τ_s, the electron spin relaxation time, for complexes of Fe^{3+}, Co^{2+}, and Ni^{2+}. These have been taken from earlier work[1–3] for complexes of edta and edtmp where variable-frequency studies were used to obtain τ_r and where τ_s was calculated from the appropriate egta complex.

For comparative purposes, average hydration numbers for complexes of ions with edta, dtpa, edtmp, and dtpmp are shown in Table 3.

(*b*) *Electronic Absorption Spectra of Complexes of* Co^{2+} *and* Ni^{2+}.—The band maxima and calculated values of *Dq* for the cobalt and nickel complexes are listed in Table 4 together with the molar absorption coefficients of the bands in the visible region. *Dq* is the ligand-field splitting parameter for an octahedral metal-ion environment. This parameter was calculated using published methods, dealing with averaged environments.[6,7] *B* values (Racah parameters) have not been calculated because of the unknown and differing degrees of distortion from octahedral symmetry. Data for the corresponding edta and edtmp complexes are included for comparison. The data for $[Co(edta)]^{2-}$ are similar to those published.[8]

(*c*) *E.S.R. Spectra of Complexes of* Cu^{2+} *and* Fe^{3+}.—Table 5 gives the e.s.r. parameters for the copper(II) complexes at two pH values. All spectra show overlapping signals of at least two species. The spectra also show a clearly split g_1 signal, which may have a few possible origins: (*i*) the presence of more than one species; (*ii*) a rhombically distorted octahedral structure of the species present; or (*iii*) the presence of a so-called overshoot line.[9] *Q*-Band e.s.r. spectra can in principle distinguish between the latter two possibilities. The values of the parameters are in all cases in agreement with a distorted octahedral co-ordination for the metal ions.[10,11]

The Figure shows e.s.r. spectra observed in the $g = 4.3$ region for the iron complexes (including those of edta and edtmp for comparison). Table 6 gives the effective *g* values together with suggested co-ordination numbers. The spectrum of $[Fe(edta)]^-$ is very similar to that reported in the literature.[12]

Table 3. Comparison of averaged hydration numbers [a] for complexes

	edta		dtpa		edtmp		dtpmp	
	b	*c*	*b*	*c*	*b*	*c*	*b*	*c*
Mn^{2+}	0.90	1.13	0	0.24	1.20	1.32	1.56	1.60
Co^{2+}	0.15	0.19	0	0.06	0.90	1.01	0.38	0.51
						(1.16) [d]		(0.72) [d]
Ni^{2+}	0.29	0.33	0.22	0.33	1.31	1.47	0.31	0.47
Cu^{2+}	0.31	0.38	0	0.10	0.77	0.97	0.65	0.88
Fe^{3+}	1.10	1.21	0.29	0.41	0.91	1.01	1.0	1.18

[a] *n* refers to the number of water molecules since hydroxyl-group formation occurs at pH > 10 for bivalent ions. For $[Fe(edta)]^-$ the value quoted is for pH 6. [b] Assuming all CO_2^- (PO_3^{2-}) bound. [c] Assuming 1 CO_2^- (PO_3^{2-}) not bound. [d] Assuming 2 PO_3^{2-} not bound.

Cotton [13] has published e.s.r. data of similar iron complexes, and related them to their probable co-ordination number. Seven-co-ordinate iron(III) complexes, like $[Fe(edta)]^-$ in water and glycerol solutions, give rise to rather sharp resonances. In contrast six-co-ordinate iron species produce a considerable splitting of the resonance. The e.s.r. spectra of the present complexes can be interpreted along these lines to determine the co-ordination numbers.

Discussion

Stability constants taken from the literature for dtpa and dtpmp complexes of ions of the first transition-metal series are shown in Table 7, together with those established for edta and edtmp. The constants for dtpa are consistently higher than those for edta for all metal ions studied. In accord with this, the measured hydration numbers for dtpa are found to be lower than for edta. Consequently, the displacement of bound

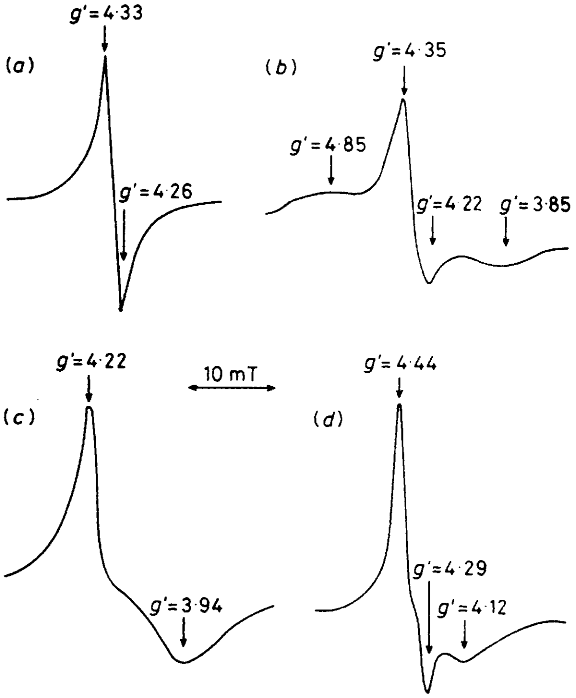


Figure. E.s.r. spectra of the iron(III) complexes in the $g' = 4.3$ region (see also Table 6): (*a*) $[Fe(edta)]^-$; (*b*) $[Fe(dtpa)]^{2-}$; (*c*) $[Fe(edtmp)]^{5-}$; (*d*) $[Fe(dtpmp)]^{7-}$

Table 4. Electronic absorption spectra of cobalt and nickel complexes in aqueous solution (absorption bands in cm^{-1}, absorption coefficients in $dm^3\ mol^{-1}\ cm^{-1}$ in parentheses, *Dq* in cm^{-1})

Complex	pH	$^4T_{1g}(F) \longrightarrow {}^4T_{2g}$	$\longrightarrow {}^4A_{2g}$	$\longrightarrow {}^4T_{1g}(P)$	*Dq*		Geometry
$[Co(edta)]^{2-}$	10	9 300	16 700 (sh)	21 100 (13.3)	1 015		Octahedral
$[Co(dtpa)]^{3-}$	10	9 400	17 200 (sh)	20 200 (17.3)	1 025		Octahedral
$[Co(dtpmp)]^{8-}$	10	8 400	15 400 (sh)	19 000 (18.8)	905		Octahedral
$[Co(edtmp)]^{6-}$	10	11 700, 12 900, 17 900 (sh), 18 900 (48), 20 200 (sh)					Five-co-ordinate?
		$^3A_{2g} \longrightarrow {}^3T_{2g}$	$\longrightarrow {}^1E_g$	$\longrightarrow {}^3T_{1g}(F)$	$\longrightarrow {}^3T_{1g}(P)$	*Dq*	
$[Ni(edta)]^{2-}$	10	10 300	12 800 (sh)	17 400 (7.5)	26 600 (11.8)	1 030	Octahedral
$[Ni(dtpa)]^{3-}$	10	9 000	12 700 (sh)	17 700 (11.3)	25 300 (15.3)	980	Octahedral
$[Ni(edtmp)]^{6-}$	10	9 400	13 300 (sh)	15 400 (6.8)	25 600 (13.5)	940	Octahedral
$[Ni(dtpmp)]^{8-}$	10	9 200	13 300 (sh)	15 700 (7.8)	24 400 (13.8)	920	Octahedral

Table 5. E.s.r. parameters of copper(II) complexes in frozen solutions of water–ethylene glycol (3 : 1 v/v) at two pH values (*A* values in 10^{-4}T in parentheses)

pH	$[Cu(dtpa)]^{3-}$	$[Cu(dtpmp)]^{8-}$
9	2.02, 2.06, 2.25 (175), 2.29 (161)	2.02, 2.07, 2.25 (169), 2.29 (143)
11	2.02, 2.06, 2.25 (175), 2.29 (161)	2.02, 2.07, 2.24 (168)

Table 6. E.s.r. parameters (effective *g* values) of iron complexes in frozen solutions of water–ethylene glycol (3 : 1 v/v) at pH 9 and probable co-ordination numbers

Complex	g'	Co-ordination number
$[Fe(edta)]^-$	4.33, 4.26	7
$[Fe(dtpa)]^{2-}$	4.85, 4.35, 4.22, 3.85	6 + 7
$[Fe(edtmp)]^{5-}$	4.22, 3.94	6
$[Fe(dtpmp)]^{7-}$	4.44, 4.29, 4.12	6

water by the ligand may contribute to the greater stability of the complexes. Trends for phosphonate compounds are less certain, despite there being much greater confidence in the more recent values of the stability constants quoted.[14] These will be discussed individually. The *X*-ray structure of the dtpa complex of Cu^{2+} has been determined.[15] This has demonstrated that all three nitrogen atoms can simultaneously co-ordinate to the metal probably accounting for a major share of its increased stability over the edta complex with two carboxyl groups unco-ordinated. Finally, it is evident from the values of *Dq* given for edta and edtmp complexes of Ni^{2+} in Table 4 that the crystal field exerted by PO_3^{2-} groups is not as large as that produced by CO_2^- groups.

dtpa Complexes.—(*a*) Mn^{2+} *and* Fe^{3+}. The most marked reduction in water binding on replacing edta with dtpa occurs with Mn^{2+} and Fe^{3+} (Table 3). Evidently, dtpa having eight potential co-ordinating groups can adapt to produce a more strain-free configuration around the metal ion with almost total elimination of primary hydration sphere water, particularly for Mn^{2+} which has a greater ionic radius (0.80 Å) compared to Fe^{3+} (0.64 Å). The e.s.r. spectrum of $[Fe(dtpa)]^{2-}$ shows it to consist of a six-co-ordinate complex (probably with no bound water molecules) and a seven-co-ordinate complex (probably with one co-ordinated water molecule) (Table 6 and Figure) resulting in the average hydration number shown in Table 3. Earlier i.r. spectroscopic investigations of an isolated $[Fe^{III}(dtpa)]^{2-}$ compound indicated [16] that only three of the five carboxyl groups are co-ordinated to the metal. This suggests that all three nitrogens are co-ordinated to iron in both complexes.

(*b*) Co^{2+}, Ni^{2+}, *and* Cu^{2+}. As with their edta counterparts, dtpa complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} have distorted-octahedral environments (Tables 4 and 5). These complexes have slightly lower hydration numbers than the corresponding edta complexes, although the increased stability constants are probably more a reflection of co-ordination of three nitrogen atoms in dtpa. Consequently, the fractional hydration numbers can be explained in terms of dynamic equilibria between a sexidentate dtpa complex and a low proportion of the monohydrated, five-co-ordinated complex. Indeed, e.s.r. spectra of the copper complexes (Table 5) clearly demonstrate the existence of two or more species in equilibrium. Furthermore, i.r. studies suggest [16] that the nickel(II) complex containing sexidentate dtpa has all three nitrogen atoms bound to Ni^{2+}.

Table 7. Stability constants ($\log_{10}$) of complexes

	edta (ref. 4)	egta [a]	dtpa (ref. 4)	edtmp	dtpmp
Mn^{2+}	14.04	12.11	15.11	12.70 [b]	11.2 [c]
Co^{2+}	16.31	12.50	19.00	17.10 [14] (15.49) [b]	15.7 [c]
Ni^{2+}	18.62	13.55	20.21	16.38 [14] (15.30) [b]	
Cu^{2+}	18.80	17.71	21.03	23.21 [14] (18.95) [b]	19.5 [12]
Fe^{3+}	25.10	20.50	28.60	>25	

[a] Stability Constants of Metal–Ion complexes, *Special Publ.*, The Chemical Society, London, 1964, no. 17. [b] M. I. Kubechnik, I. M. Dyatlova, T. A. Medved, Yu F. Begulin, and V. V. Gidorenko, *Proc. Acad. Sci. USSR*, 1967, **175**, 621. [c] Technical Bulletin IC/SCS-322, Monsanto Industrial Chemicals Co., St. Louis, Missouri.

dtpmp Complexes.—(*a*) Mn^{2+}, Ni^{2+}, *and* Co^{2+}. The hydration number of the dtpmp complex of Mn^{2+} is the highest of all the metal complexes investigated (Table 3). This is not entirely unexpected since Mn^{2+} does have the lowest charge to radius ratio and does not particularly have a strong affinity for nitrogen donors. Similarly, the hydration number of Mn^{2+} in complexes containing directly bound water increases in the series dtpa < edta < edtmp < dtpmp, consistent with the opposing trend in stability constants.

The Co^{2+} complex of dtpmp appears to adopt a distorted-octahedral geometry similar to the edta and dtpa counterparts (Table 4). This is in sharp contrast with the edtmp complex, whose absorption spectrum suggests a much more distorted structure. The spectrum of the $[Co(edtmp)]^{6-}$ complex resembles that of complexes having a five-co-ordinate trigonal-bipyramidal structure.[17,18] A seven-co-ordinate geometry may also be possible, although the agreement with published spectral data [19,20] is less convincing. However, such a structure may be more in accord with the observed hydration number * and the fairly high stability constant. The molar absorption coefficient of this complex is larger than for octahedral complexes due to the lower symmetry of the complex. Complex formation with edtmp is only complete above pH 8, thus explaining the lower calculated molar absorption coefficient at pH 7. However, it cannot be ruled out that, even at pH 9—10, there is still a fraction of the complex present as an octahedral cobalt species, which is not detected due to the relatively low absorption of such a complex. The dtpmp complex is found to be less hydrated than the edtmp complex but more hydrated than the dtpa complex (Table 3). As anticipated, this is probably a consequence of simultaneous binding of three nitrogen donors which (*i*) firmly anchor the ligand onto the metal ion, (*ii*) minimise repulsion between co-ordinated ligand groups, and (*iii*) facilitate octahedral geometry. Overall, it seems likely that a dynamic equilibrium persists between sexidentate dtpmp with which Co^{2+} accommodates three PO_3^{2-} groups in its co-ordination sphere and a five-co-ordinated complex containing one water molecule and only two PO_3^{2-} groups. This is reinforced by the observation of a slight pH dependence of the absorption coefficient of $[Co(dtpmp)]^{8-}$, suggesting a mixture of two species. The Ni^{2+} complex of dtpmp similarly adopts a

---

* Where there are changes in co-ordination number, changes in metal–water proton distances may become significant. Consequently, whereas most hydration numbers are accurate to about 10%, that for $[Co(edtmp)]^{6-}$ is accurate to 10—30%.

distorted-octahedral environment (Table 4). Again a dynamic equilibrium between two species is anticipated.

(*b*) Fe^{3+} *and* Cu^{2+}. In contrast to the other ions, the hydration number of the dtpmp complex of Fe^{3+} is not very different from that of the edtmp complex. Both adopt a distorted-octahedral geometry (Table 6). Since Fe^{III} has no preference for N over O donor atoms it can be envisaged that $[Fe^{III}(dtpmp)]^{7-}$ has a very similar structure to $[Fe^{III}(edtmp)]^{5-}$.

The dtpmp complex of Cu^{2+} has only a slightly lower hydration number than its edtmp complex. Like the dtpa complexes, the dtpmp complexes have six-co-ordinate geometries and probably have similar structures with dynamic equilibria between species containing one or no water molecules. Consistent with this view, several species can be detected in the e.s.r. spectrum of the $[Cu(dtpmp)]^{8-}$ complex (Table 5).

Acknowledgements

The authors thank A. A. Memelink for recording electronic absorption and e.s.r. spectra, J. Rockliffe for measurement of relaxation times, O. Laurie for preparation of samples, and E. G. Smith, J. G. Chambers, D. Cummins, and Professor J. Reedijk (State University of Leiden, The Netherlands) for helpful discussions.

References

1 J. Oakes and E. G. Smith, *J. Chem. Soc., Faraday Trans. 2*, 1981, 299.
2 J. Oakes and E. G. Smith, *J. Chem. Soc., Faraday Trans. 1*, 1983, 543.
3 J. Oakes and E. G. Smith, *J. Chem. Soc., Dalton Trans.*, 1983, 601.
4 S. Chaberek and A. E. Martell, 'Organic Sequestering Agents,' Wiley, New York, 1959.
5 H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
6 J. Reedijk, P. W. N. M. van Leeuwen, and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1968, **87**, 129.
7 J. Reedijk, W. L. Driessen, and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 1095.
8 E. F. K. McCandlish, T. K. Michael, J. A. Neal, E. C. Lingafelta, and N. J. Rose, *Inorg. Chem.*, 1978, **17**, 1383.
9 R. D. Bereman and D. J. Kosman, *J. Am. Chem. Soc.*, 1977, **99**, 7322.
10 B. J. Hathaway and D. E. Billing, *Co-ord. Chem. Rev.*, 1970, **5**, 143.
11 B. J. Hathaway, M. J. Bew, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc. A*, 1969, 2312.
12 G. Lang, R. Aasa, K. Garbett, and R. J. P. Williams, *J. Chem. Phys.*, 1971, **55**, 4539.
13 S. A. Cotton, *Chem. Phys. Lett.*, 1976, **41**, 606.
14 R. J. Motekaitis, I. Murase, and A. E. Martell, *Inorg. Chem.*, 1976, **15**, 2305.
15 R. C. Seccombe, B. Lee, and G. M. Henry, *Inorg. Chem.*, 1975, **14**, 1147.
16 R. E. Sievers and J. C. Bailar, *Inorg. Chem.*, 1962, **1**, 174.
17 J. Reedijk, J. C. Jansen, H. van Koningsveld, and C. G. van Kralingen, *Inorg. Chem.*, 1978, **17**, 1990.
18 I. Bertini, P. Dapporto, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, 1975, **14**, 1639.
19 M. Gerloch, I. Morgenstern-Badarau, and J.-P. Audiere, *Inorg. Chem.*, 1979, **18**, 3220.
20 M. Gerloch and L. R. Hanton, *Inorg. Chim. Acta*, 1981, **49**, 37.

Received 20*th July* 1983; *Paper* 3/1239