Anomalous Solution Behaviour of Isomorphous Complexes of Zirconium- and Hafnium-(IV)†

(the late) Dennis F. Evans, Gerard W. Griffiths, Caroline O'Mahoney, David J. Williams,* Chih Y. Wong and J. Derek Woollins
The Evans and Chemical Crystallography Laboratories, Department of Chemistry, Imperial College, London SW7 2AY, UK

The synthesis of [Zr^{IV}(egta)] and [Hf^{IV}(egta)] in aqueous solution, where H_4egta = ethylenedioxydiethylenedinitrilotetraacetic acid, is reported. The eight-co-ordinate complexes have been characterised by X-ray crystallography, ^1H NMR spectroscopy, mass spectrometry and elemental analysis. The two compounds are isostructural in the solid state. Solution studies by ^1H NMR spectroscopy show that the hafnium analogue has a higher degree of symmetry. In particular, the spectrum of the zirconium complex reveals all of the methylene groups to be inequivalent whereas in the hafnium complex the $-N(CH_2CO_2)_2-$ and the $-NCH_2CH_2O-$ methylene groups show increased magnetic equivalence.

Group 4 transition-metal complexes have a high tendency towards hydrolysis in aqueous solution. In some studies these hydrolysed species have been identified, in others hydrolysis has been avoided by careful control of pH. The under-developed aqueous chemistry is further limited by the insolubility of the initial products. Most zirconium minerals contain 1 to 5% hafnium whose chemistry is almost identical. In fact, of all the elements, zirconium and hafnium are two of the most difficult to separate.

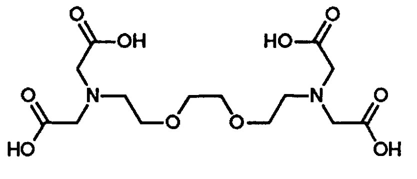
The complexes of ethylene dioxydiethylenedinitrilotetraacetic acid (H_4egta) with alkaline-earth metal ions have been studied.[1] It was shown that the egta^{4-} ligand has a high selectivity for Ca^{2+} over Mg^{2+} (by $\approx 10^6$) which is even larger than that typically exhibited by calcium-binding proteins. The X-ray structures of $[Ca(egta)]^{2-}$ and $[Cd(egta)]^{2-}$ confirm the octadenticity of the egta^{4-} ligand. The co-ordination geometry about both the calcium and cadmium remain approximately dodecahedral. The M–O(ether) bond lengths were found to be longer than the M–O(carboxylate) bond lengths, indicative of the weaker donor nature of the ether oxygens.

Intorre and Martell[2] have studied a series of zirconium complexes in aqueous solution and have concluded, on the basis of potentiometric titrations, that the ether oxygens in egta^{4-} are too 'soft' for discrete [Zr(egta)] to form. The role of the ether oxygens in metal complexes has been studied by dynamic NMR spectroscopy;[3] both ether oxygen co-ordination and non-co-ordination occurs depending on the metal ion involved.

Here, we describe the synthesis of [Zr(egta)] and [Hf(egta)] in aqueous solution. The complexes have been studied by X-ray crystallography, mass spectrometry and elemental analysis. Solution ^1H NMR studies reveal differences in their solution structures.

Experimental

General.—The compound $ZrOCl_2{\cdot}8H_2O$ was purified by dissolution of the crude yellow oxychloride (25 g, 77.6 mmol) in hydrochloric acid (2.0 mol dm^{-3}, 100 cm^3). The solution was heated to 70 °C and filtered. White crystals of pure $ZrOCl_2{\cdot}8H_2O$ were isolated on cooling and washed with cold ethanol–hydrochloric acid (1:1). Yield: 9.4 g, 38%. The compound $HfOCl_2{\cdot}8H_2O$ was obtained commercially and used without further purification.



H_4egta

Proton NMR spectra were recorded on a JEOL EX270 (270 MHz) or a Bruker AM500 (500 MHz) spectrometer in D_2O. Chemical shifts are quoted relative to internal sodium 3-trimethylsilylpropane-1-sulfonate. Microanalyses were carried out by MEDAC Ltd. Mass spectra were recorded on a VG AutospecQ spectrometer in the liquid secondary ion (LSIMS$^+$) mode with the sample suspended in an aqueous glycerol matrix.

Preparation of $[Zr(egta)]{\cdot}3H_2O$ **1**.—Zirconium dichloride oxide octahydrate (1.00 g, 3.10 mmol) was dissolved in water (10 cm^3) in a centrifuge tube. Ammonium hydroxide solution (specific gravity 0.880) was added to the stirred solution until precipitation was complete. The white precipitate was centrifuged and washed with water repeatedly to remove the excess of ammonia (10 to 15 times). The wet solid, $Zr(OH)_4$, was transferred to a suspension of H_4egta (1.20 g, 3.15 mmol) in water (30 cm^3) and refluxed for 72 h. The clear solution was reduced in volume and cooled to aid crystallisation. Colourless crystals of $[Zr(egta)]{\cdot}3H_2O$ were filtered off and dried in a desiccator over anhydrous calcium chloride. Yield: 0.65 g, 40% (Found: C, 32.25; H, 4.95; N, 5.35. $[Zr(egta)]{\cdot}3H_2O$ requires C, 32.25; H, 5.00; N, 5.35%). Mass spectrum: m/z 467, corresponds to $[^{90}Zr(egta)H]^+$.

Preparation of $[Hf(egta)]{\cdot}3H_2O$ **2**.—The preparation of $[Hf(egta)]{\cdot}3H_2O$ was analogous to the zirconium derivative with $Hf(OH)_4$ prepared from $HfOCl_2{\cdot}8H_2O$ (1.00 g, 2.44 mmol). The wet solid was refluxed with H_4egta (0.94 g, 2.47 mmol) for 18 h. Yield: 1.09 g, 73% (Found: C, 27.20; H, 4.05;

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

N, 4.45. [Hf(egta)]·$3H_2O$ requires C, 27.60; H, 4.30; N, 4.60%). Mass spectrum: m/z 557, corresponds to $[^{180}Hf(egta)H]^+$.

X-Ray Crystallography.—The complexes [Zr(egta)]·$3H_2O$ and [Hf(egta)]·$3H_2O$ were both recrystallised from clear aqueous solutions by slow evaporation at ambient temperature.

[Zr(egta)]·$3H_2O$ **1**.—*Crystal data.* $C_{14}H_{26}N_2O_{13}Zr$, $M = 521.6$, monoclinic, space group $P2_1/a$, $a = 13.085(5)$, $b = 9.631(4)$, $c = 16.440(8)$ Å, $\beta = 110.03(3)°$, $U = 1946$ Å^3, $Z = 4$, $D_c = 1.78$ g cm^{-3}, Cu-Kα radiation, $\bar{\lambda} = 1.541\ 78$ Å, μ(Cu-Kα) = 53 cm^{-1}, $F(000) = 1072$.

Data collection and processing. Nicolet *R*3*m* diffractometer, Cu-Kα radiation (graphite monochromator) using ω scans. 2584 Independent reflections were measured ($2\theta < 116°$), of which 2472 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; a numerical absorption correction (face-indexed crystal) was applied. Maximum and minimum transmission factors 0.784 and 0.235 respectively.

Structure analysis and refinement. The structure was solved by the heavy-atom method. The non-hydrogen atoms were refined anisotropically. The protons on the three water molecules were located from a ΔF map and refined isotropically subject to a distance constraint of 0.98 Å. The positions of the remaining hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters, [U(H) = 1.2 U_{eq}(C)], and allowed to ride on their parent carbon atoms. Refinement was by block-cascade, full-matrix least squares to give R 0.067, R' 0.069 [$w^{-1} = \sigma^2(F) + 0.000\ 30F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 2.81 and −2.13 e Å^{-3} respectively. The mean and maximum shift/error in the final refinement were 0.014 and 0.179 respectively.

[Hf(egta)]·$3H_2O$ **2**.—*Crystal data.* $C_{14}H_{26}HfN_2O_{13}$, $M = 608.9$, monoclinic, space group $P2_1/a$, $a = 13.076(2)$, $b = 9.631(2)$, $c = 16.441(4)$ Å, $\beta = 110.12(2)°$, $U = 1944$ Å^3, $Z = 4$, $D_c = 2.08$ g cm^{-3}, Cu-Kα radiation, $\bar{\lambda} = 1.541\ 78$ Å, μ(Cu-Kα) = 106 cm^{-1}, $F(000) = 1200$.

Data collection and processing. Nicolet *R*3*m* diffractometer, Cu-Kα radiation (graphite monochromator) using ω scans. 2632 Independent reflections were measured ($2\theta < 116°$), of which 2594 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; a numerical absorption correction (face-indexed crystal) was applied. Maximum and minimum transmission factors 0.462 and 0.095 respectively.

Structure analysis and refinement. Structure solution and refinement were as above. Refinement converged to give R 0.033, R' 0.036 [$w^{-1} = \sigma^2(F) + 0.000\ 54F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 2.21 and −1.23 e Å^{-3} respectively. The mean and maximum shift/error in the final refinement were 0.041 and 0.379 respectively.

Computations for both structures were carried out on an IBM 386/70 computer using SHELXTL PC.[4]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Atomic co-ordinates (× 10^4) for [Zr(egta)]·$3H_2O$

Atom	*x*	*y*	*z*
Zr	1132(1)	349(1)	2546(1)
N(1)	456(4)	−1953(5)	2607(3)
N(2)	2427(4)	1898(5)	3544(3)
O(1)	690(3)	140(5)	3634(3)
O(2)	876(3)	−1097(5)	4826(3)
O(3)	−439(3)	164(5)	1567(3)
O(4)	−2058(4)	−833(6)	994(3)
O(5)	1473(3)	−1000(5)	1517(3)
O(6)	1955(3)	1580(5)	1751(3)
O(7)	2578(3)	−712(5)	3224(3)
O(8)	3908(4)	−1176(5)	4459(3)
O(9)	429(3)	2337(4)	2479(3)
O(10)	270(4)	4406(5)	3010(4)
C(1)	752(5)	−2326(7)	3541(4)
C(2)	768(4)	−1035(7)	4062(4)
C(3)	−756(5)	−1919(7)	2207(4)
C(4)	−1128(5)	−807(7)	1514(4)
C(5)	948(5)	−2941(7)	2151(4)
C(6)	919(6)	−2325(7)	1295(4)
C(7)	1661(6)	−317(8)	804(5)
C(8)	2431(6)	836(9)	1204(5)
C(9)	2566(5)	2807(7)	2179(4)
C(10)	3179(5)	2450(7)	3102(4)
C(11)	3092(5)	1068(7)	4297(4)
C(12)	3245(5)	−378(6)	3999(4)
C(13)	1810(5)	3024(7)	3779(4)
C(14)	769(5)	3331(7)	3049(4)
O(15)	−3646(4)	958(7)	−15(4)
O(16)	3314(4)	−3915(6)	3939(4)
O(17)	−4838(5)	−1393(9)	−780(4)

Table 2 Atomic co-ordinates (× 10^4) for [Hf(egta)]·$3H_2O$

Atom	*x*	*y*	*z*
Hf	1144(1)	343(1)	2549(1)
N(1)	472(3)	−1956(4)	2611(2)
N(2)	2428(3)	1893(3)	3548(2)
O(1)	699(3)	160(3)	3630(2)
O(2)	879(3)	−1087(3)	4823(2)
O(3)	−409(3)	173(3)	1565(2)
O(4)	−2042(3)	−834(4)	984(2)
O(5)	1482(3)	−997(3)	1526(2)
O(6)	1952(2)	1572(3)	1760(2)
O(7)	2583(2)	−724(3)	3223(2)
O(8)	3917(3)	−1181(3)	4455(2)
O(9)	425(2)	2327(3)	2464(2)
O(10)	264(3)	4404(3)	3016(3)
C(1)	750(4)	−2322(4)	3537(3)
C(2)	772(3)	−1022(4)	4063(3)
C(3)	−740(3)	−1919(5)	2199(3)
C(4)	−1119(3)	−799(5)	1509(3)
C(5)	955(3)	−2943(4)	2152(3)
C(6)	931(4)	−2334(5)	1307(3)
C(7)	1658(5)	−310(5)	802(3)
C(8)	2424(4)	844(5)	1201(3)
C(9)	2567(4)	2813(5)	2181(3)
C(10)	3169(3)	2451(5)	3106(3)
C(11)	3094(4)	1053(4)	4298(3)
C(12)	3257(4)	−394(4)	3995(3)
C(13)	1808(3)	3011(4)	3781(3)
C(14)	767(4)	3319(5)	3047(3)
O(15)	1682(3)	1073(3)	6069(3)
O(16)	1348(3)	4051(4)	−21(3)
O(17)	−184(4)	3565(6)	758(3)

Results and Discussion

The X-ray structures of complexes **1** and **2** (Tables 1–3; Fig. 1) show no noticeable differences in their co-ordination geometries. All of the analogous bond lengths are the same within 3σ (Table 3). The largest differences in the co-ordination angles are for O(3)–M–O(6) and for O(7)–M–O(9) (*ca.* 1°). Both complexes are eight-co-ordinate utilising all of the available co-ordination sites of the ligand. The co-ordination geometry is distorted square antiprismatic [the basal planes comprising N(2), O(5), O(6), O(7) and N(1), O(1), O(3), O(9)]. The co-ordination polyhedron (Fig. 3) is a distorted dodecahedron which is virtually identical to those of the calcium and cadmium egta complexes.[1] Furthermore, the relative arrangements of the carboxyl groups with respect to the hafnium and

Table 3 Selected comparative bond lengths (Å) and angles (°) for [Hf(egta)]·$3H_2O$ and [Zr(egta)]·$3H_2O$ (M = Hf or Zr)

	Hf	Zr		Hf	Zr
M–N(1)	2.397(4)	2.402(5)	M–N(2)	2.419(3)	2.426(5)
M–O(1)	2.060(4)	2.069(5)	M–O(3)	2.123(3)	2.140(4)
M–O(5)	2.280(3)	2.296(5)	M–O(6)	2.268(4)	2.288(5)
M–O(7)	2.096(3)	2.104(4)	M–O(9)	2.113(3)	2.110(4)
N(1)–M–N(2)	136.1(1)	136.2(2)	N(1)–M–O(1)	70.6(1)	70.0(2)
N(2)–M–O(1)	78.6(1)	79.2(2)	N(1)–M–O(3)	72.1(1)	71.5(2)
N(2)–M–O(3)	145.4(1)	145.9(2)	O(1)–M–O(3)	99.8(1)	99.3(2)
N(1)–M–O(5)	71.1(1)	71.0(2)	N(2)–M–O(5)	125.8(1)	125.4(2)
O(1)–M–O(5)	140.6(1)	139.9(2)	O(3)–M–O(5)	76.8(1)	77.1(2)
N(1)–M–O(6)	139.1(1)	138.9(2)	N(2)–M–O(6)	73.5(1)	73.2(2)
O(1)–M–O(6)	149.7(1)	150.4(2)	O(3)–M–O(6)	96.7(1)	97.6(2)
O(5)–M–O(6)	68.1(1)	67.9(2)	N(1)–M–O(7)	78.5(1)	78.9(2)
N(2)–M–O(7)	69.9(1)	69.3(2)	O(1)–M–O(7)	88.3(1)	87.8(2)
O(3)–M–O(7)	144.6(1)	144.7(2)	O(5)–M–O(7)	75.3(1)	75.4(2)
O(6)–M–O(7)	92.8(1)	92.3(2)	N(1)–M–O(9)	132.6(1)	132.8(2)
N(2)–M–O(9)	71.1(1)	70.6(2)	O(1)–M–O(9)	83.3(1)	83.6(2)
O(3)–M–O(9)	74.4(1)	75.4(2)	O(5)–M–O(9)	131.2(1)	131.8(2)
O(6)–M–O(9)	77.0(1)	77.4(2)	O(7)–M–O(9)	140.9(1)	140.0(2)

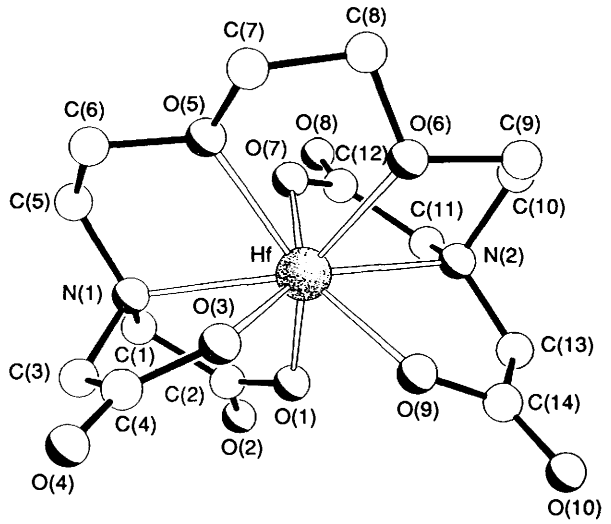


Fig. 1 The X-ray structure of [Hf(egta)] in **2**

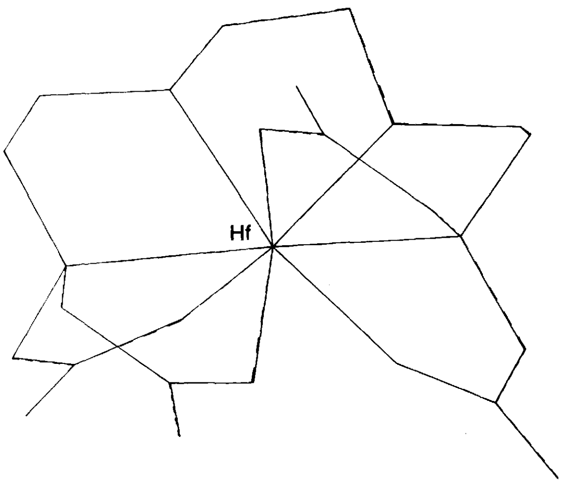


Fig. 2 The least-squares fit for [Zr(egta)] and [Hf(egta)]

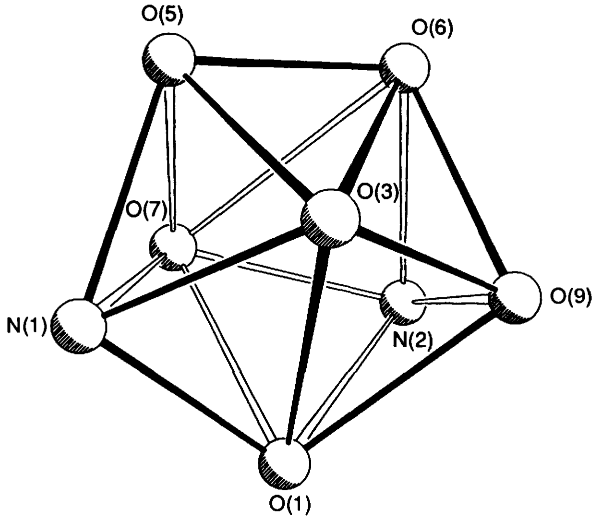


Fig. 3 The co-ordination polyhedron of [Hf(egta)]

zirconium centres are also the same as that exhibited by the calcium and cadmium complexes. One $N(CH_2CO_2)_2$ unit co-ordinates with an essentially *cis* MO_2 geometry whereas the other $N(CH_2CO_2)_2$ unit has effectively *trans* MO_2 geometry (Fig. 1) [The O(1)–Hf–O(3) and O(7)–Hf–O(9) angles are 99.8(1) and 140.9(1)° respectively]. The co-ordination distances for both nitrogen and oxygen do not differ markedly from those previously reported for zirconium.[5] As expected, the two M–O(ether) bond lengths are significantly longer (by *ca.* 0.17 Å) than the M–O(carboxylate) bond lengths. The bite angles of adjacent co-ordinating centres within the ligand are in the range 68.1(1)° for O(5)–Hf–O(6) to 73.5(1)° for N(2)–Hf–O(6).

The 500 MHz ^1H NMR spectra of **1** (Fig. 4) and **2** (Fig. 5) show several similarities and have been assigned on the basis that the octadentate complex remains essentially square antiprismatic in solution as described in the solid state above. The ^1H NMR spectra were recorded at two different fields (270 MHz and 500 MHz) to verify genuine chemical shift assignments against spin–spin coupling assignments. The overall assignments of complexes **1** and **2** are summarised pictorially in Fig. 6 and Fig. 7 respectively.

For **1**, there are three types of methylene groups in the complex which are separated in the NMR spectra. The protons deriving from the $-OCH_2CH_2O-$ group are attributed to the high-field resonances (δ 3.40–3.60). The rigidity of the $-OCH_2CH_2O-$ chelate ring in solution is supported by the observed AA′BB′ multiplicity pattern. It is well known that second-order effects become significant when the difference in chemical shift, Δδ, approaches below about six times the

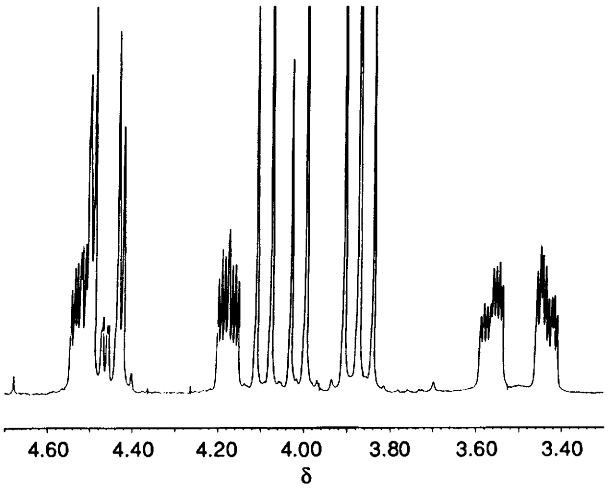


Fig. 4 ^1H NMR (500 MHz, D_2O) spectrum of [Zr(egta)]

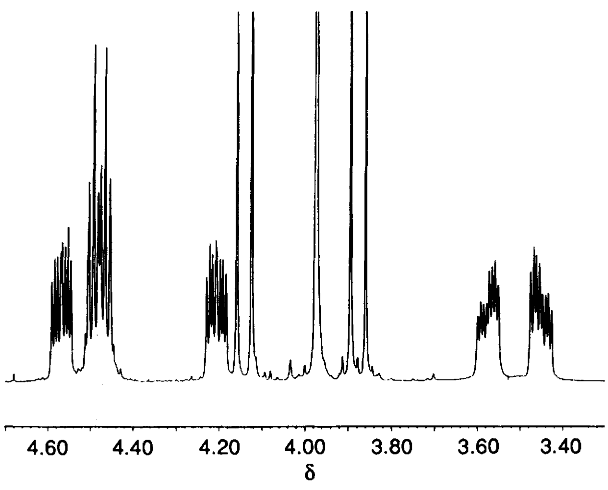


Fig. 5 ^1H NMR (500 MHz, D_2O) spectrum of [Hf(egta)]

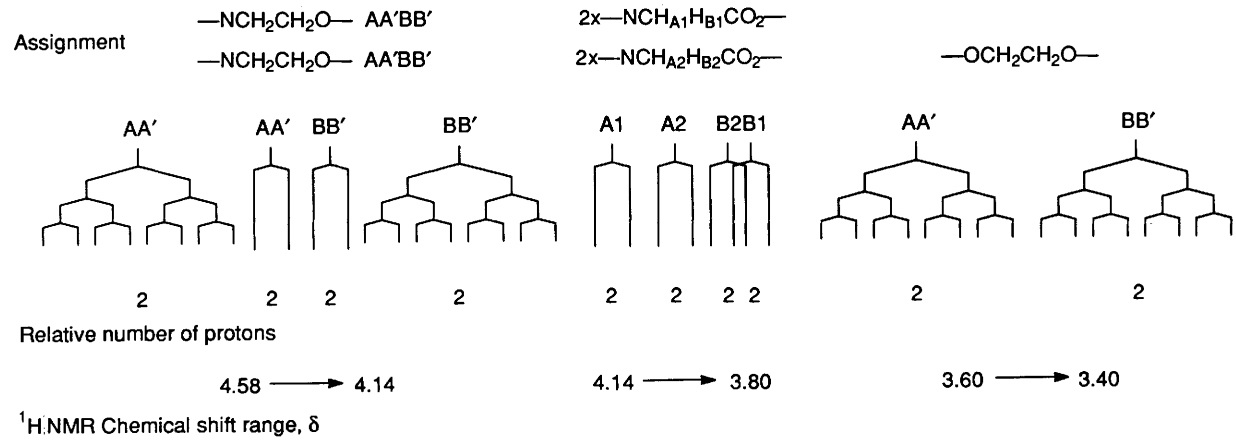


Fig. 6 Pictorial representation of ^1H NMR analysis of [Zr(egta)]

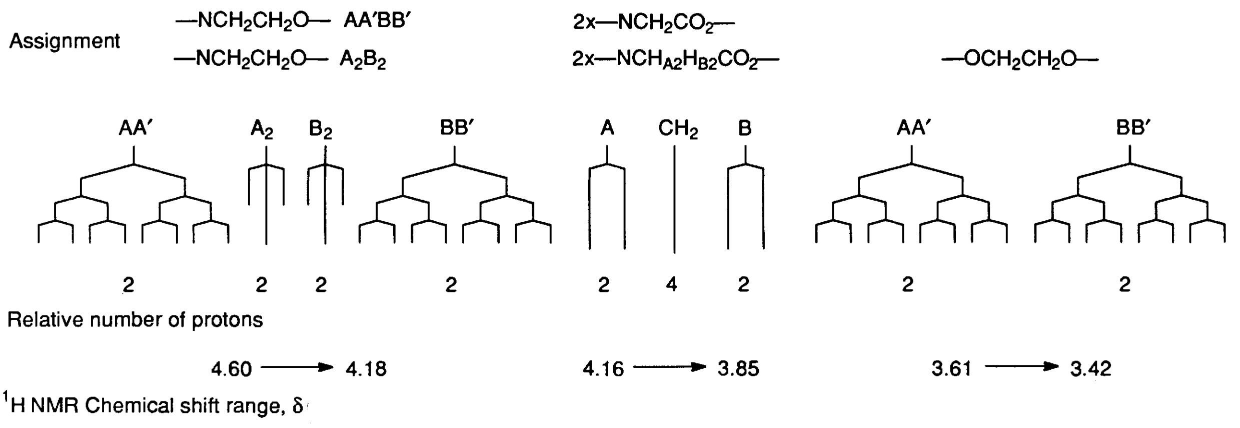


Fig. 7 Pictorial representation of ^1H NMR analysis of [Hf(egta)]

coupling between the two nuclei. The difference in chemical shift between AA′ and BB′ ($\Delta\delta$ = 60 Hz at 500 MHz) is just over four times the $^2J_{AB}$ coupling ($^2J_{AB}$ = 13.8, $^3J_{AB'}$ = 7.1 and $^3J_{AA'}$ = 3.6 Hz), and therefore consistent with the non-first order spectrum observed.

The four $-NCH_2CO_2-$ groups exhibit magnetic equivalences corresponding to C(1), C(3) and C(11), C(13) and give rise to two sets of AB pairs at δ 3.80–4.14, but due to complicated overlap the assignment is shown more clearly in the 270 MHz spectrum (Fig. 8). The second-order nature of the resonances is again observed due to the small $\Delta\delta$ ($\Delta\delta$ = 65 and 36 Hz at 270 MHz with $^2J_{AB}$ = 17.2 and 17.5 Hz respectively). The two different $-N(CH_2CO_2)_2-$ units observed in solution reflect the difference between *cis*- and *trans*-MO_2 geometries as described in the solid state but individual assignment cannot be made.

The two $-NCH_2CH_2O-$ groups give rise to a more complicated system (δ 4.14–4.58). If we consider two different $-NCH_2CH_2O-$ chelators, one $-NCH_2CH_2O-$ set may be considered as another AA′BB′ system (δ 4.18 and 4.52, $\Delta\delta$ = 170 Hz at 500 MHz, $^2J_{AB}$ = 12.3, $^3J_{AB'}$ = 7.3 and $^3J_{AA'}$ = 3.6

Fig. 8 ^1H NMR (270 MHz, D_2O) spectrum of $-NCH_2CO_2-$ groups in [Zr(egta)]

Hz). It is interesting that in this case, $\Delta\delta > 6J$ and thus demonstrates minimal second-order contribution. The other $-NCH_2CH_2O-$ may be rationalised as another AA′BB′ system but with reduced resolution. The NCH_2 protons are assigned to the resonance at δ 4.50 and OCH_2 to the resonance at δ 4.43, $^3J_{AB}$ = 6.0 Hz. The difference between the two $-NCH_2CH_2O-$ groups may be the consequence of the adjacent *cis* and *trans* $-N(CH_2CO_2)_2-$ units. In the solid state all of the $-CH_2CH_2-$ groups exhibit a staggered conformation.

The assignment of the $-OCH_2CH_2O-$ group in **2** is analogous to that in **1**. For the $-NCH_2CO_2-$ chelate again two sets of resonances are noted, but in this case only one set is an AB pair. The other two $-NCH_2CO_2-$ groups give rise to a simple singlet indicating magnetic equivalence. Further magnetic equivalence is observed for a set of $-NCH_2CH_2O-$ protons (δ 4.45–4.51) where simple triplets ($^3J_{AB}$ = 5.5 Hz) indicate simply two different methylene groups coupling to each other. The majority of the spectrum of **2** resembles that observed for **1** with only small changes in chemical shift and even smaller changes in spin–spin couplings. The increased magnetic equivalence of some methylene groups in **2** indicates that although the complexes are isostructural there is a difference in the strength of bonding reflected by the degree of free rotation of these methylene groups. We speculate that the differences in the solution properties of **1** and **2** arise as a consequence of two possible processes *i.e.* changes in the C–N–C angles with the two pairs of $N(CH_2CO_2)_2$ units and/or slight adjustments in the M–N bond lengths.

Equimolar amounts of both complexes when mixed in D_2O give a spectrum which is an overlap of both isolated complexes. This indicates that the increased flexibility in **2** was not an effect due to different concentrations, pH or temperature. The spectra for the two complexes showed the same differences in $(CD_3)_2SO$. Furthermore, variable-temperature experiments on **1** showed no change in the spectrum up to 75 °C. Our observations underline the sensitivity of NMR measurements to minor structural changes (*cf.* solid-state X-ray studies).

Previous attempts to synthesise **1** and **2** have failed principally because there is a high kinetic energy barrier required to form the otherwise thermodynamically stable [Zr(egta)] and [Hf(egta)] complexes. This reflects the difficulties involved in obtaining accurate stability parameters of these systems where the true equilibrium may not be easily established. The synthetic strategy involved does, however, provide a convenient method for further study of possible zirconium- and hafnium-(IV) complexes which are stable in aqueous solution.

Acknowledgements

We are grateful to the SERC for an equipment grant. We also thank Mr. R. N. Sheppard for the 500 MHz NMR spectra and Mr. J. N. Bilton for the mass spectra. One of us (C. Y. W.) thanks the SERC for a grant.

References

1 C. K. Schauer and O. P. Anderson, *J. Am. Chem. Soc.*, 1987, **109**, 3646.
2 B. I. Intorre and A. E. Martell, *J. Am. Chem. Soc.*, 1960, **82**, 358.
3 P. Mirti and M. C. Gennaro, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3221.
4 SHELXTL PC Version 4.2, Siemens X-Ray Analytical Instruments, 1991.
5 T. E. MacDermott, *Coord. Chem. Rev.*, 1973, **11**, 1.

Received 20*th March* 1992; *Paper* 2/01483A