Fig. s1a
supplem. material

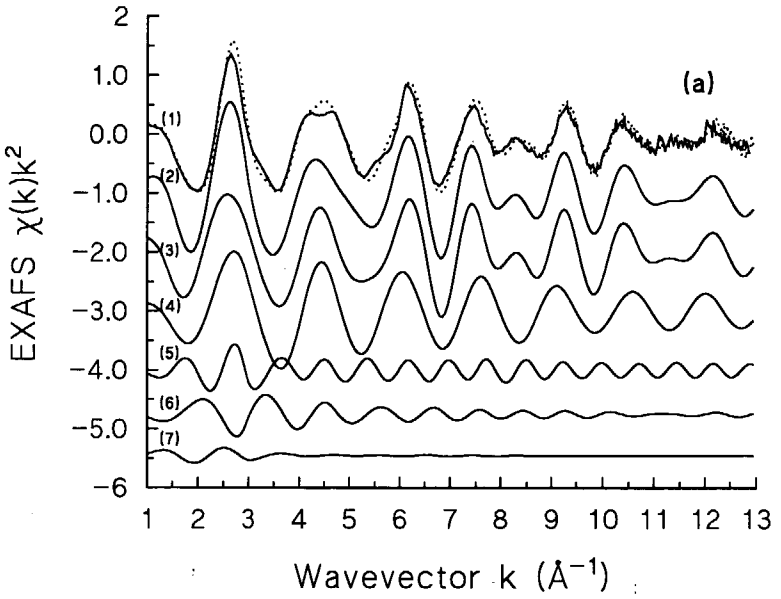

Figure S1.a

Comparison of the theoretical (the cluster of 32 atoms around the Gd) and experimental XAFS signals $\chi(\kappa)\kappa^2$ for the GdH(oep)(tpp) complex: experimental signal at LT (1); all SS contributions within the cluster (2); all SS and MS contributions within the cluster (3); all SS contributions of the first shell (4); all SS contributions of the second and third shells (5); all DS contributions within the cluster (6); all TS contributions within the cluster (7). All spectra are plotted on the same vertical scale and displaced vertically for clarity. Finally, the spectrum of Gd(III)(oep)$_2$ complex (1) is also given (dotted line).

Fig 5.16
Suppl. material

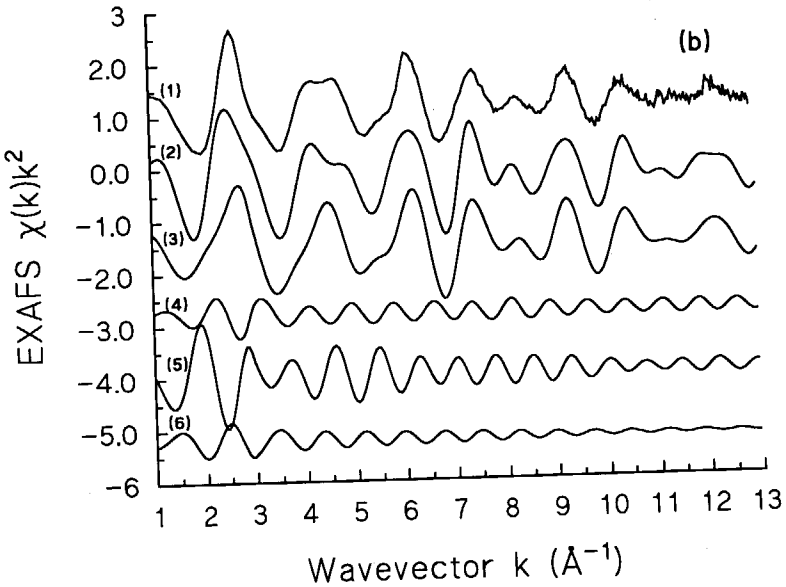

Figure S1.b Comparison of the theoretical (the cluster of 48 atoms around the Gd) and experimental XAFS signals $\chi(\kappa)\kappa^2$ for the GdH(oep)(tpp) complex: experimental signal at LT (1); all SS contributions within the cluster (2); all SS and MS contributions within the cluster (3); all SS contributions of the forth shell (4); all DS contributions of the fourth shell (5); all TS contributions of the fourth shell (6). All spectra are plotted on the same vertical scale and displaced vertically for clarity.

Fig. S2a
Supplementary

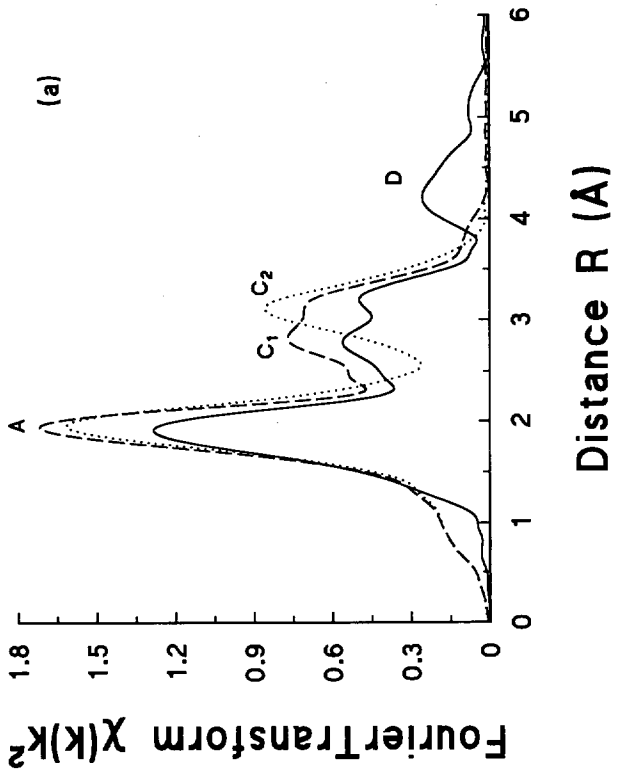

Figure S2.a Comparison of the theoretical (the cluster of 32 atoms around the Gd) and experimental FT of XAFS signals for the GdH(oep)(tpp) complex: experimental signal at LT (solid line); all SS contributions within the cluster (dashed line); all SS and MS contributions within the cluster (dotted line).

Fig. S2b
Suppl. material

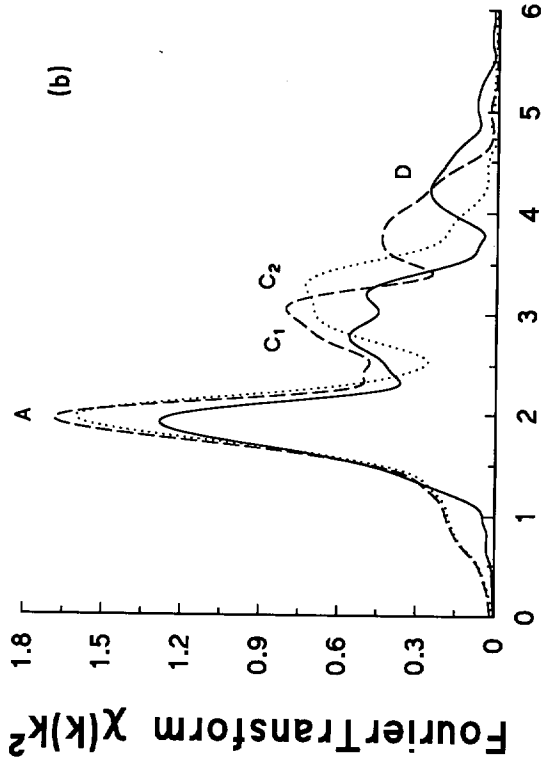

Figure S2.b Comparison of the theoretical (the cluster of 48 atoms around the Gd) and experimental FT of XAFS signals for the GdH(oep)(tpp) complex: experimental signal at LT (solid line); all SS contributions within the cluster (dashed line); all SS and MS contributions within the cluster (dotted line).

Table S.1. First coordination shell structural data obtained from the best-fit analysis with the theoretical phases and amplitudes label (feff) including the asymmetry of RDF (C_3 cumulant). N is the number of atoms located at the distance R from the Ln, σ^2 is the DW factor, C_3 is the cumulant, ε is the fitting error. The absolute errors are ±0.5 on N, ± 0.02 Å on R, and ± 0.001 Å^2 on σ^2. This error bars are lowered when we compare different measurements to ±0.3 on N, ± 0.005 Å on R, and ± 0.001 Å^2 on σ^2.

	Bonds Ln-N (EXAFS)					Bonds Ln-N (XRD)	
State	N_1	R_1 (Å)	σ_1^2 (Å^2)	$C_3 \times 10^{-4}$	$\varepsilon \times 10^{-3}$	R_{av} (Å)	R_{N7}(Å)
			Gd(III)(oep)$_2$				
LT(feff)	8.0	2.50	0.004	3.0	3.2	2.50	
LT(feff)[a]	8.0	2.48	0.004	1.5	3.1	2.50	
LT(feff)[a]	8.0	2.47	0.004	0.0	3.1	2.50	
RT(feff)	8.2	2.51	0.004	5.1	3.4	2.50	
RT(feff)[a]	8.1	2.48	0.006	1.1	3.0	2.50	
RT(feff)[a]	8.1	2.48	0.006	0.0	3.1	2.50	
			Gd(III)H(oep)(tpp)				
LT(feff)	7.1	2.49	0.005	4.1	3.0	2.532	2.516[b]
LT(feff)[a]	7.0	2.48	0.005	2.6	2.5	2.532	2.516[b]
LT(feff)[a]	7.0	2.47	0.005	0.0	2.9	2.532	2.516[b]
RT(feff)	7.1	2.49	0.007	1.8	2.5	2.538	2.523[b]
RT(feff)[a]	6.9	2.47	0.006	0.9	2.4	2.538	2.523[b]
RT(feff)[a]	6.9	2.47	0.006	0.0	2.4	2.538	2.523[b]
			GdH(tpp)$_2$				
LT(feff)	6.3	2.50	0.006	6.0	2.0		
LT(feff)[a]	6.2	2.48	0.006	4.1	1.7		
LT(feff)[a]	6.2	2.47	0.006	0.0	2.2		
RT(feff)	6.4	2.51	0.008	8.7	2.2		
RT(feff)[a]	6.2	2.48	0.008	4.3	1.7		
RT(feff)[a]	6.2	2.47	0.008	0.0	2.1		
			Sm(III)(oep)$_2$				
RT(feff)	8.0	2.53	0.006	7.1	3.2	2.53	
RT(feff)[a]	8.0	2.50	0.006	2.4	2.6	2.53	
RT(feff)[a]	8.0	2. 49	0.006	0.0	2.8	2.53	
			Sm(III)H(oep)(tpp)				
RT(feff)	6.7	2.53	0.006	9.5	1.7	2.550	2.542[b]
RT(feff)[a]	6.7	2.50	0.006	4.9	1.4	2.550	2.542[b]
RT(feff)[a]	6.6	2.49	0.006	0.0	1.8	2.550	2.542[b]
			Sm(III)H(tpp)$_2$				
RT(feff)	6.5	2.53	0.006	10.9	2.2		
RT(feff)[a]	6.4	2.50	0.006	5.7	1.5		
RT(feff)[a]	6.4	2.49	0.006	0.0	2.1		

[a] The mean bond lengths Ln-N are calculated from the crystallographic data on the Eu(III)(oep)$_2$ complex from ref. 1, according to an increase in the ionic radii of Ln^{3+}.

[b] The mean bond lengths for the seven shortest Ln-N distances are calculated from the crystallographic data on the Ln(III)H(oep)(tpp) crystals ref. 15,16.