

²⁷Al NMR studies on complexation of
aluminium with
N-(2'-hydroxyethyl)iminodiacetic acid,
N,N-bis(2'-hydroxyethyl)glycine and
triethanolamine

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The utility of ²⁷Al NMR in characterisation of metal chelates of Al is demonstrated in the case of N-(2'-hydroxyethyl)iminodiacetic acid (HEIDA). Based on the near linear relationship between ²⁷Al chemical shift and denticity of ligand reported earlier for Al chelates with aminopolycarboxylic acids, it could be concluded that HEIDA functions as a tetradentate ligand with participation of hydroxyethyl group in coordination. N,N-Bis(2'-hydroxyethyl)glycine (DHEG) does not complex with Al while triethanolamine (TEA) functions as a bidentate ligand in a limited pH range.

We have reported in an earlier communication¹ the usefulness of ²⁷Al NMR in characterising complex species of Al. We have shown the existence of a nearly linear relationship between ²⁷Al chemical shift and denticity of the ligand in aluminium chelates with aminocarboxylic acids containing 2 to 6 donor sites. This relationship was found to be useful in determining the change in denticity of the aminopolycarboxylic acid in the Al chelate on varying the pH of the aqueous solution. HEIDA is generally a tridentate ligand but can function as tetra-coordinating ligand if the hydroxyethyl group takes part in coordination. Probable coordination through the -CH₂CH₂OH group has been reported in the case of Fe(III) and rare earth complexes of HEIDA²⁻⁴. In the present paper we report the ²⁷Al NMR studies of complexation of aluminium with HEIDA(H₂L), DHEG(HL) and TEA(L).

Experimental

AlCl₃ solution was prepared from reagent grade AlCl₃.6H₂O and standardized by EDTA titration using xylenol orange as indicator. Ligands were

obtained from Sigma Chemical Co. Stock solutions of the complexes were prepared by mixing AlCl₃ solution and ligand in the required molar ratios. The pH of the mixtures was adjusted with either NaOH or HCl.

²⁷Al NMR spectra

The ²⁷Al NMR spectra were recorded on a Varian XL 300 spectrometer operating at 78.157 MHz (pulse width, 15-27 μs; flip angle, 90°; acquisition time, 1s; digital resolution, 0.97 Hz per point; 16000 data points; spectral width, 8000 Hz, 50-2500 transients; line broadening, 2-20 Hz). Samples were taken in 10 mm NMR tubes with a concentric 5 mm tube containing C₆D₆ for locking. All the chemical shifts are relative to external [Al(H₂O)₆]³⁺ (in H₂O containing 20% D₂O) as reference.

Results and discussion

The complex species existing at different pH values were identified from ²⁷Al NMR data using the nearly linear relationship between ²⁷Al chemical shift of the normal complex and denticity of the ligand reported earlier¹. The ligands used in the present work contain one or more -CH₂-CH₂OH groups linked to the nitrogen [N-(2'-hydroxyethyl)iminodiacetic acid [(HOOCCH₂)₂NCH₂CH₂OH]; N,N-bis(2'-hydroxyethyl)glycine [(CH₂CH₂OH)₂NCH₂COOH]; triethanolamine [(CH₂CH₂OH)₃N]]. Replacement of two water molecules in the octahedral [Al(H₂O)₆]³⁺ by ligand atoms in glycine leading to the formation of [(H₂O)₄Al-N-CH₂COO]²⁺ results in deshielding by ≈ 8 ppm. Each additional chelate ring gives rise to deshielding in the range 7-10 ppm. Since no data have been reported on deshielding by chelation through -N-CH₂CH₂OH group, it is assumed that the chemical shift is nearly the same as that for chelation through -N-CH₂COOH group. The ²⁷Al NMR data for the three systems are summarised in Table 1, and NMR spectra for Al-HEIDA system are given in Fig 1. The results of Al³⁺ complexation are discussed in detail below.

$^*\text{C}_{\text{Al}}$	$\text{C}_{\text{L}}/^*\text{C}_{\text{Al}}$	pH	$\delta^{27}\text{Al}$ (ppm)	$\text{W}_{1/2}$ (Hz)
Ligand = HEIDA				
0.05	1	2.0	0.12	68
"	1	2.0	24.95	59
"	1	4.1	0.05	39
"	1	4.1	24.70	127
"	1	6.0	24.65	225
"	2	4.0	0.05	39
"	2	4.0	25.00	98
"	2	7.0	26.50	940
Ligand = DHEG				
0.1	1	2.5	0.12	10
"	1	4.3	0.13	39
"	1	5.6	0.05	137
"	1	5.6	62.90	78
Ligand = TEA				
0.1	1	2.5	0.1	10
"	1	4.0	4.2 (Sh)	
			62.90	19
"	1	5.0	0.13	49
			62.90	20

$^*\text{C}_{\text{Al}}$ = total concentration of Al (mol dm^{-3})

C_{L} = total concentration of ligand (mol dm^{-3}).

N-(2'-Hydroxyethyl)iminodiacetic acid (H_2L)

The ^{27}Al NMR spectrum of a 1:1 mixture of AlCl_3 and HEIDA displayed two peaks at δ 0.12 and 24.95 ppm, the former due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ being much more intense compared to the latter due to complex species. On increasing the pH to 4.1, major part of Al was converted to complex species. With further increase in pH to 6.0 the signal due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ disappeared and that due to complex species was observed at δ 24.65 ppm. The solution at pH 6.0 was faintly turbid which could be due to partial hydrolysis. However no resonance was observed due to the hydroxo complex $[\text{Al}_3(\text{OH})_{24}\text{O}_4(\text{H}_2\text{O})_{12}]^{7+}$ at 63 ppm⁵. On raising the $\text{C}_{\text{L}}/\text{C}_{\text{Al}}$ ratio to 2, the behaviour of the system was almost the same. The complex species formed with HEIDA could be characterised by comparison with chelating abilities of iminodiacetic acid (IDA) and nitrilotriacetic acid (NTA) with Al. In the absence of coordination of hydroxyethyl group to Al, HEIDA is expected to function as a tridentate ligand similar to IDA with a signal at δ 18 ppm. On the contrary, if it acts as a tetradentate ligand the anticipated chemical shift will be in the vicinity of δ 25.4 ppm as observed in the case of Al-NTA chelate. Since the observed signal is $\approx$ 25 ppm, it can be concluded that HEIDA functions as a tetradentate ligand.

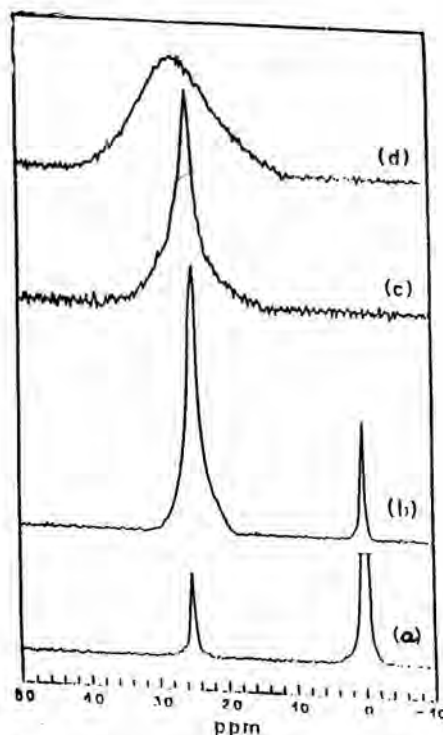


Fig 1- ^{27}Al NMR spectra of 1:1 (a,b & c) and 1:2 (d) Al HEIDA at pH 2(a), 4.1(b), 6(c) & 7(d).

Absence of formation of the 1:2 chelate with HEIDA can also be attributed to the functioning of this ligand as a tetradentate since Al does not form a 1:2 chelate with NTA. Just as the NTA chelate, the HEIDA chelate has a reasonably high degree of symmetry ($\text{W}_{1/2}$ 100-130 Hz compared to 40 Hz for the NTA chelate). The complexes reported earlier which exhibit coordination of hydroxyethyl group of HEIDA are its complexes with Fe (III)⁴ and rare earths³.

N,N-Bis (2'-hydroxyethyl)glycine (HL)

This ligand is expected to function as a tetradentate if both the hydroxyethyl groups take part in coordination. However the ^{27}Al NMR spectra showed that no complexation took place with Al. In the pH range 2-4 the ^{27}Al NMR spectra showed only one peak due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ while at pH 5.6 formation of $[\text{Al}_3(\text{OH})_{24}\text{O}_4(\text{H}_2\text{O})_{12}]^{7+}$ with peak at δ 62.9 ppm was favoured. This species is the interlayer aluminium polynuclear component of the pillared clays utilised in catalytic processes⁶. Hence the AlCl_3 -DHEG system may find application in the preparation of pillared clays. In addition to the resonance at δ 62.9 ppm a broad peak ($\text{W}_{1/2}$ 137Hz) due to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ was also

present at 0.05 ppm. This indicates considerable chemical exchange between $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and the polynuclear species.

Triethanolamine (L)

In the absence of carboxylic acid group, TEA can complex only with metal ions having very strong affinity to oxygen donors. Complexation with Al was absent at *pH* 2.5. On raising the *pH* to 4, in addition to the major resonance at 0.1 ppm, a shoulder at 4.2 ppm and a sharp peak at 62.9 ppm were observed. The shoulder may be attributed to a complex species in which TEA acts as a bidentate ligand. At *pH* 4.9 the solution was slightly turbid. No complex species was present. The major part of Al was in the form of $[\text{Al}_{13}(\text{OH})_{24}\text{O}_4(\text{H}_2\text{O})_{12}]^{7+}$

along with $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. AlCl_3 -triethanolamine system can also be used in pillaring work.

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