Nuclear Magnetic Resonance Studies of Complexes of Aluminium(III), Gallium(III), and Indium(III) with Disulphonated 2,2′-Dihydroxyazobenzene Ligands in Aqueous Solution

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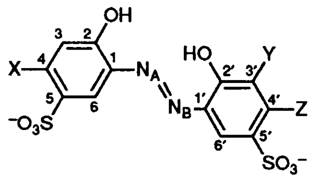
Proton n.m.r. spectra are reported for complexes of Al^{III}, Ga^{III}, and In^{III} with a variety of 5,5′-disulphonated 2,2′-dihydroxyazobenzenes in D_2O solution. Ligand exchange is slow on an n.m.r. time-scale, and both 1 : 1 and 1 : 2 complexes have been characterized. The spectra of the complexes of Al^{III} and Ga^{III} show that the metal ions are bound to only one of the nitrogens of the azo groups. In contrast, the 1 : 2 indium(III) complexes of the two symmetric ligands studied are fluxional, and values of $\Delta G^{\ddagger}$ are given for the process which 'flips' the metal ions between the two nitrogen atoms. For the 1 : 1 and 1 : 2 aluminium(III) and the 1 : 2 gallium(III) complexes of asymmetric ligands, the expected isomers have been observed, and the equilibrium isomer ratios are reported. Assignments based on ^1H n.m.r. spectra have been confirmed by the ^{15}N n.m.r. spectrum of a 1 : 2 gallium(III) complex with a ligand enriched in ^{15}N. The isomer ratios can be largely rationalized by considering the effect substituents in the 4 and 4′ positions have on the electron density of the remote nitrogen atom in the azo groups. The effect of changes in pD on the isomer ratios and the ^1H chemical shifts has also been studied for the 1 : 2 gallium(III) complexes of a ligand with an ionizable 4′-OH group.

Compounds containing the 2,2′-dihydroxyazobenzene grouping have been used for many years as dyestuffs,[1] and also as reagents in the compleximetric and spectrophotometric determination of a variety of metal ions.[2] Although in certain metal compounds the azo group acts as an η^2 ligand,[3] the available evidence indicates that in 2,2′-dihydroxyazobenzene-metal complexes the ligands are normally tridentate with the metal bound to one of the nitrogens only. For the non-labile complexes of asymmetrically substituted 2,2′-dihydroxyazobenzenes with Co^{III}, Pd^{II}, and Pt^{II}, Swiss workers have isolated the isomers expected for co-ordination in this manner, and have studied their ^1H,[4,5] ^{13}C,[5] and ^{15}N[6] n.m.r. spectra in organic solvents.

The present work is concerned with the ^1H n.m.r. spectra (in D_2O solution) of the complexes of Al^{III}, Ga^{III}, and In^{III} with the water soluble ligands shown in the Scheme. A new type of fluxional behaviour has been characterized with the indium(III) complexes of the two symmetrical 2,2′-dihydroxyazobenzenes. For the complexes of Al^{III} and Ga^{III} with the asymmetric ligands it has been possible to obtain quantitative information concerning the isomeric distribution in the equilibrium mixtures.



Ligand	X	Y	Z
[a] H_2L^1 (dhabs)	H	H	H
H_2L^2	Me	H	Me
H_2L^3	H	H	OH
H_2L^4	Me	H	OH
H_2L^5	H	Me	OH
H_2L^6	F	Me	OH
H_2L^7	Cl	Me	OH
H_2L^8	Me	Me	OH
H_2L^9	MeO	Me	OH
H_2L^{10}	H	C_4H_4[b]	
H_2L^{11}	Me	C_4H_4[b]	

Scheme. Ligands studied. [a] As disodium salts, hence in solution H_2L^1, *etc.*, will have a dinegative charge. [b] Naphthalene ring. The numbering system used for the naphthalene ring is different from that shown; OH is 1′ and N=N is 2′

Experimental

Preparation of Intermediates and Ligands.—2-Aminophenol-4-sulphonic acid (aps) was obtained from Aldrich as a jet black powder, and was recrystallized from water (activated charcoal) to give almost colourless cubes.

2-*Amino*-5-*fluorophenol*-4-*sulphonic acid.* 5-Fluoro-2-nitrophenol (Aldrich, 7.5 g, 0.048 mol) was added in small portions, with manual stirring, to fuming H_2SO_4 (30% SO_3, 7 cm^3) at 0—5 °C. The mixture was left overnight at room temperature (r.t.), and poured onto ice–water (100 cm^3). The suspension was filtered, concentrated HCl (20 cm^3) and $SnCl_2 \cdot H_2O$ (30 g, 0.133 mol) added, and the mixture stirred at 70—80 °C for 30 min. After cooling to 0 °C the solid was filtered off, washed with ice-cold 2 mol dm^{-3} HCl followed by ice-cold water. The moist solid was stirred with water (80 cm^3) and 0.880 sp. gr. NH_3 added until an almost clear solution was obtained. This was filtered, and excess of concentrated HCl added to the filtrate. After cooling to 0 °C the solid was filtered off, washed with a little ice-cold water, then diethyl ether, and dried at 90 °C. Yield 1.3 g (13%).

2-*Amino*-5-*chlorophenol*-4-*sulphonic acid.* 2-Amino-5-chlorophenol[7] (1.0 g, 0.007 mol) was added to fuming H_2SO_4 (30% SO_3, 4 cm^3), the mixture left overnight at r.t., and then poured onto ice (20 g). The solid was filtered off, washed with ice-cold water, and dried *in vacuo* at 90 °C. Yield 1.5 g (96%).

6-*Amino*-m-*cresol*-4-*sulphonic acid.* 6-Amino-*m*-cresol (10 g,

Table 1. ^1H N.m.r. data (δ) for complexes of Al^{III}, Ga^{III}, and In^{III} with ligands L^1 and L^2 in D_2O

Complex	H^3	$H^{3'}$	H^4	$H^{4'}$	H^6	$H^{6'}$	Me	Me′
$[AlL^1]^-$	7.02_0	6.99_7	7.81_4	*	8.29_3	8.24_7		
$[AlL^1{}_2]^{5-}$	6.78_6	6.73_6	7.75_9	7.69_3	8.35_7	8.34_9		
$[GaL^1]^-$	7.70_4	7.07_5	7.84_1	7.75_8	8.30_0	8.29_0		
$[GaL^1{}_2]^{5-}$	6.84_1	6.77_2	7.78_4	7.68_4	8.40_3	8.33_9		
$[InL^1]^-$	7.06_6	7.03_4	7.78_1	7.73_3	8.31_3			
$[InL^1{}_2]^{5-}$	6.90_0	6.79_3	7.75_0	7.61_5	8.36_7	8.31_9		
$[AlL_2]^-$	6.88_0	6.83_8			8.27_9	8.26_7	2.58_9	2.58_1
$[AlL^2{}_2]^{5-}$	6.64_1	6.57_2			8.37_2	8.35_4	2.53_8	2.49_5
$[GaL^2{}_2]^{5-}$	6.68_5	6.60_4			8.41_7	8.33_3	2.54_7	2.50_1
$[InL^2{}_2]^{5-}$	6.75_9	6.65_6			8.40_8	8.34_6	2.54_6	2.50_5

* Overlap with $[AlL^1{}_2]^{5-}$ and free-ligand peaks.

0.081 mol) and concentrated H_2SO_4 (30 cm^3) were heated at 70—80 °C for 1 h, the mixture cooled and poured onto ice. The crude product was filtered off, washed with water, and dissolved in dilute aqueous NaOH. The solution was stirred for 30 min with activated charcoal, filtered, and the filtrate acidified with concentrated HCl. The solid was filtered off, washed with water, and dried. Yield 15.3 g (93%).

2-*Amino*-3-*methoxyphenol*-4-*sulphonic acid.* 2-Hydroxy-4-methoxyazobenzene[8] (5 g, 0.022 mol) and concentrated H_2SO_4 (17 cm^3) were kept at r.t. overnight. The mixture was poured into water (50 cm^3) and Na_2CO_3 added to pH *ca.* 3.5, followed by NaCl (10 g). The precipitated sodium 2-hydroxy-4-methoxyazobenzene-5-sulphonate was filtered off, washed with 20% aqueous NaCl, a little ice-cold water, and then EtOH. Yield 4.6 g (64%). This compound (3.75 g, 0.011 mol) was dissolved in water (150 cm^3) at 80 °C, and $Na_2S_2O_4$ added in portions with stirring until the orange colour was discharged. Stirring was continued for 20 min to allow the excess of $Na_2S_2O_4$ to oxidize. After cooling to 0 °C, excess of concentrated HCl was added and the solid filtered off, washed with water, and dried. Yield 0.91 g (38%).

Sodium resorcinol-4-*sulphonate.* An intimate mixture of resorcinol (25 g, 0.23 mol) and concentrated H_2SO_4 (12.6 cm^3, 0.23 mol) was kept at r.t. for 2 d, and then added to water (100 cm^3). After the addition of Na_2CO_3 to pH 5, the solution was extracted three times with an equal volume of diethyl ether to remove residual resorcinol, and evaporated to dryness. The residue was finely powdered and stirred with ethanol–water (3:1, 100 cm^3). The extract was evaporated to dryness. Yield 15.8 g (33%).

Sodium 2-*methylresorcinol*-4-*sulphonate.* This was prepared as above from 2-methylresorcinol in 54% yield. The ^1H n.m.r. spectrum of the product in D_2O showed the presence of 8 mol% of 2-methylresorcinol-4,6-disulphonate, which did not interfere with the subsequent stage.

Sodium m-*cresol*-4-*sulphonate. m*-Cresol (25 g, 0.32 mol) and concentrated H_2SO_4 (17.8 cm^3, 0.32 mol) were heated at 110 °C for 1 h, cooled, poured into water (100 cm^3), and Na_2CO_3 added to pH 5. After extraction with diethyl ether to remove residual *m*-cresol the solution was evaporated to dryness. The residue was finely powdered, and heated at 90 °C for 1 d. The ^1H n.m.r. spectrum in D_2O showed the presence of approximately equal amounts of the 4- and 6-sulphonates. The desired isomer was obtained by stirring the powder with absolute ethanol (250 cm^3) for 20 h, filtering, evaporating the filtrate to dryness, and drying the residue at 90 °C. Yield 9.9 g (15%).

All the above intermediates were characterized by their ^1H n.m.r. spectra in D_2O or D_2O–NaOD.

Ligand H_2L^1 (disodium 2,2′-dihydroxyazobenzene-5,5′-disulphonate dhabs) was prepared from 2,2′-dihydroxyazobenzene (Aldrich) as described by Süs,[9] recrystallized from water, and dried *in vacuo* at 90 °C. ^1H N.m.r. (D_2O): δ 7.02_5 (2 H, d, H^3), 7.70_7 (2 H, dd, H^4), and 8.21_2 (2 H, d, H^6).

Ligand H_2L^2. 2,2′-Dihydroxy-4,4′-dimethylazobenzene (0.73 g, 0.003 mol) and concentrated H_2SO_4 (5 cm^3) were heated at 60 °C for 30 min. After cooling, the mixture was poured onto ice (15 g) and centrifuged. To the centrifugate was added NaCl (3 g), the precipitate filtered off, washed with a little ice-cold water, and recrystallized from EtOH–water. Yield 0.95 g (71%) (Found: C, 37.05; H, 2.80; N, 6.45. $C_{14}H_{12}N_2Na_2O_8S_2$ requires C, 37.65; H, 2.70; N, 6.30%). ^1H N.m.r. (D_2O): δ 2.46_7 (6 H, s, Me^4), 6.60_0 (2 H, s, H^3), and 8.11_6 (2 H, s, H^6).

Ligand H_2L^5. The compound aps (3.8 g, 0.02 mol) was dissolved in 1.0 mol dm^{-3} aqueous NaOH (20 cm^3) and $NaNO_2$ (1.4 g, 0.02 mol) in water (5 cm^3) added. The solution was cooled to 0—5 °C, and concentrated HCl (7 cm^3) added over 15 min. This diazonium solution was added to sodium 2-methylresorcinol-4-sulphonate (4.52 g, 0.02 mol) and Na_2CO_3 (6 g, 0.057 mol) in water (50 cm^3). The reaction mixture was kept at 6—8 °C for 1 d, acidified with concentrated HCl, and NaCl (5 g) added. After filtration and washing with 20% aqueous NaCl followed by a little ice-cold water the crude product was recrystallized from water. Yield 1.5 g (17%) (Found: C, 34.40; H, 2.15; N, 6.10. $C_{13}H_{10}N_2Na_2O_9S_2$ requires C, 34.85; H, 2.25; N, 6.25%). ^1H N.m.r. (D_2O): δ 1.87_6 (3 H, s, $Me^{3'}$), 6.91_4 (1 H, d, H^3), 7.61_0 (1 H, dd, H^4), 7.90_0 (1 H, s, $H^{6'}$), and 8.05_4 (1 H, d, H^6).

The asymmetric ligands H_2L^3, H_2L^4, and H_2L^6—H_2L^{11} were prepared in a similar manner. ^1H N.m.r. (D_2O): H_2L^3, δ 6.91_5 (1 H, d, H^3), 7.57_8 (1 H, dd, H^4), 8.04_5 (1 H, s, $H^{6'}$), and 8.60_2 (1 H, s, H^6); the $H^{3'}$ resonance was not observed since almost complete deuteriation occurred in the D_2O solution; H_2L^4, δ 2.46_6 (3 H, s, Me^4), 6.57_1 (1 H, s, H^3), 8.02_9 (1 H, s, H^6 or $H^{6'}$), and 8.06_8 (1 H, s, $H^{6'}$ or H^6); as with H_2L^3, the $H^{3'}$ resonance was not observed as a consequence of rapid deuteriation; H_2L^6, δ 1.89_7 (3 H, s, $Me^{3'}$), 6.67_3 [1 H, d, $^3J(^{19}F-^1H) = 11.74$, H^3], 7.88_4 (1 H, s, $H^{6'}$), and 8.02_4 (1 H, d, $^4J(^{19}F-^1H) = 8.04$ Hz, H^6]; H_2L^7, δ 1.86_2 (3 H, s, $Me^{3'}$), 6.90_8 (1 H, s, H^3), 7.89_1 (1 H, s, $H^{6'}$), and 8.15_1 (1 H, s, H^6); H_2L^8, δ 1.80_4 (3 H, s, $Me^{3'}$), 2.47_3 (3 H, s, Me^4), 6.63_3 (1 H, s, H^3), 7.85_1 (1 H, s, $H^{6'}$), and 8.01_9 (1 H, s, H^6); H_2L^9, δ 1.80_0 (3 H, s, $Me^{3'}$), 6.31_4 (1 H, s, H^3), 7.77_8 (1 H, s, $H^{6'}$), and 7.93_1 (1 H, s, H^6); H_2L^{10}, δ 6.57_7 (1 H, d, H^3), 7.13_9 (1 H, t, $H^{7'}$), 7.21_3 (1 H, dd, H^4), 7.35_9 (1 H, t, $H^{6'}$), 7.79_2 (1 H, d, $H^{8'}$), 7.80_8 (1 H, s, $H^{3'}$), 8.01_7 (1 H, d, H^6), and 8.02_0 (1 H, d, $H^{5'}$); H_2L^{11}, δ 2.24_6 (3 H, s, Me^4), 6.33_4 (1 H, s, H^3), 7.18_1 (1 H, t, $H^{8'}$), 7.41_3 (1 H, t, $H^{6'}$), 7.78_5 (1 H, d, $H^{8'}$), 7.86_6 (1 H, s, H^4), 8.05_8 (1 H, d, $H^{5'}$), and 8.10_6 (1 H, s, $H^{3'}$).

The ligand H_2L^7 with ^{15}N in the B position was prepared from $Na^{15}NO_2$, obtained by neutralizing 40% HNO_3 (98% ^{15}N) with NaOH, evaporating to dryness, and heating the residue with lead shot in a stainless-steel crucible at 410 °C[10]

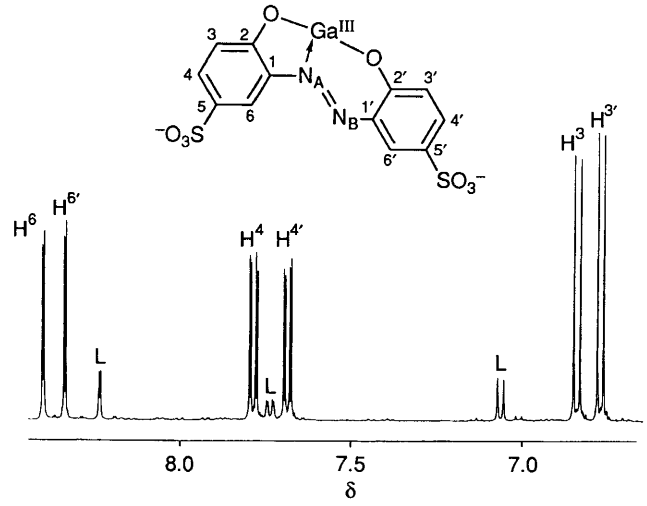


Figure 1. ^{1}H N.m.r. spectrum (500 MHz, D_2O) of $[GaL^1{}_2]^{5-}$ ($[Ga^{III}]_t$ = 0.022, $[L^1]_t$ = 0.057 mol dm^{-3}, pD = 7.4); L = free ligand. The structure depicted shows only one of the equivalent ligands of the 2:1 complex

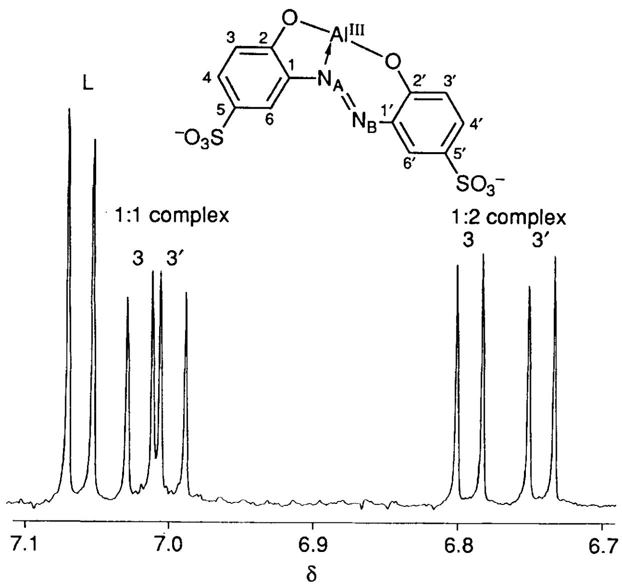


Figure 2. ^{1}H N.m.r. spectrum for H^3 (500 MHz, D_2O) of a solution containing $[Al^{III}]_t$ = 0.020, $[L^1]_t$ = 0.050 mol dm^{-3}, pD 4.4; L = free ligand. The structure depicted shows only one of the equivalent ligands of the 2:1 complex

(fusible metal bath). After dissolving in water, the solution was analysed for nitrite by $KMnO_4$.[11] The ^{1}H n.m.r. spectrum was as for the normal ligand, except that H$^{6'}$ was a doublet, with $J(^{15}N-^1H)$ = 2.69 Hz.

Physical Measurements.—Proton n.m.r. spectra were recorded on Bruker WM250 (250 MHz), JEOL GSX270 (270 MHz), and Bruker WM500 (500 MHz) spectrometers; ^{15}N n.m.r. spectra on a Bruker WH500 spectrometer at 50.7 MHz. A 2 mol dm^{-3} $^{15}NH_4Cl$ solution in D_2O was used as a secondary reference (δ 25 p.p.m. relative to liquid $^{15}NH_3$).

Solutions of the complexes were prepared by dissolving appropriate amounts of the ligand and $AlK(SO_4)_2{\cdot}12H_2O$, $Ga(NO_3)_3{\cdot}xH_2O$, or $InCl_3{\cdot}4H_2O$ in D_2O, and adjusting the pD with NaOD in D_2O. The pD values were calculated from the relationship pD = pH + 0.40, where pH is the reading measured on the pH meter.[12] For the asymmetric ligands, the solutions were allowed to stand at 25 °C for at least 24 h (Al^{III}) or 12 h (Ga^{III}), to allow equilibrium to be attained between the isomers.

Results and Discussion

Symmetrical Ligands H_2L^1 (dhabs) *and* H_2L^2.—Figure 1 presents the ^{1}H n.m.r. spectrum of a D_2O solution containing Ga^{III} and H_2L^1 in the molar ratio 1:2.6. The presence of free-ligand peaks shows that ligand exchange is slow on an n.m.r. time-scale, and from the relative intensities it is clear that a 1:2 complex $[GaL^1{}_2]^{5-}$ has been formed. Separate resonances are observed for the two aromatic rings in each ligand, confirming that the ligands are asymmetrically co-ordinated as shown. The assignments given in Figure 1 and Table 1 are based partly on two-dimensional correlation spectroscopy (COSY) and partly on the ^{1}H n.m.r. spectra previously reported[13] for the 1:2 complexes of Al^{III} and Ga^{III} with the related ligand where the N=N group in dhabs has been replaced by C=N. Here, the largest low-field shifts in complex formation are observed for protons in the aromatic ring bound to the N atom. The assignments are also consistent with the ^{1}H n.m.r. spectra[4,5] of the complexes of Co^{III}, Pd^{II}, and Pt^{II} with asymmetrical 2,2′-dihydroxyazobenzenes,[4] and with the ^{15}N n.m.r. spectrum described below.

A similar ^{1}H n.m.r. spectrum with two additional CH_3 resonances was observed for a D_2O solution (pD 7.4) containing Ga^{III} (0.025 mol dm^{-3}) and H_2L^2 (0.05 mol dm^{-3}). A difference nuclear Overhauser enhancement (n.O.e.) spectrum showed that the Me group giving rise to the low-field resonance was in the same ring as the aromatic hydrogens which also resonated at low field. The ^{1}H n.m.r. spectra of the $[AlL^1{}_2]^{5-}$ and $[AlL^2{}_2]^{5-}$ complexes were quite similar to these obtained for the corresponding gallium(III) species (Table 1).

For D_2O solutions with $[M^{III}]$ = 0.020—0.025 and $[H_2L^1]$ = 0.05 mol dm^{-3} the 1:2 complexes were the predominant species over the approximate pD range 5—11 (Al^{III}) and 3.7—11 (Ga^{III}). At lower pD values, where the concentration of $(L^1)^{4-}$ is quite small, 1:1 complexes were formed. Figure 2 shows the ^{1}H n.m.r. spectrum of the Al^{III}–H_2L^1 system at pD 4.4, where resonances characteristic of the free ligand, the 1:1 complex, and the 1:2 complex are all present. The slow ligand exchange observed under these conditions is noteworthy. It can be seen that the 1:1 complex exhibits the same asymmetric ligand binding as does the 1:2 complex. Lower pD values were required to form appreciable amounts of the 1:1 complex of Ga^{III} with H_2L^1. For example with $[Ga^{III}]$ = 0.020, $[H_2L^1]$ = 0.050 mol dm^{-3}, and at a pD of 1.5, *ca.* 92% of the Ga^{III} was present as the 1:1 complex, together with the free ligand. Under these conditions none of the 1:2 complex could be detected.

Rather different n.m.r. behaviour to that described above is observed with the 1:2 complex of In^{III} and H_2L^1. Figure 3 shows the variable-temperature ^{1}H n.m.r. spectra of a D_2O solution (pD 7.4) containing In^{III} and H_2L^1 in the molar ratio 1:2.5. At low temperatures, the spectrum of the $[InL^1{}_2]^{5-}$ complex is very similar to that found with Al^{III} and Ga^{III}. As the temperature is raised the resonances from the two aromatic rings broaden, then coalesce, and finally at high temperatures the two rings apparently become equivalent. Since the free-ligand resonances remain reasonably sharp throughout, it is clear that intermolecular exchange does not contribute appreciably to these phenomena. In addition, the line shapes at a given temperature were, within experimental error, unchanged when the pD was increased to 8.4. This suggests that H$^+$ attack on an In–O bond is not involved, and that the complex is genuinely fluxional, with the indium(III) cation 'flipping' between N$_A$ and N$_B$. A possible mechanism for this involving a

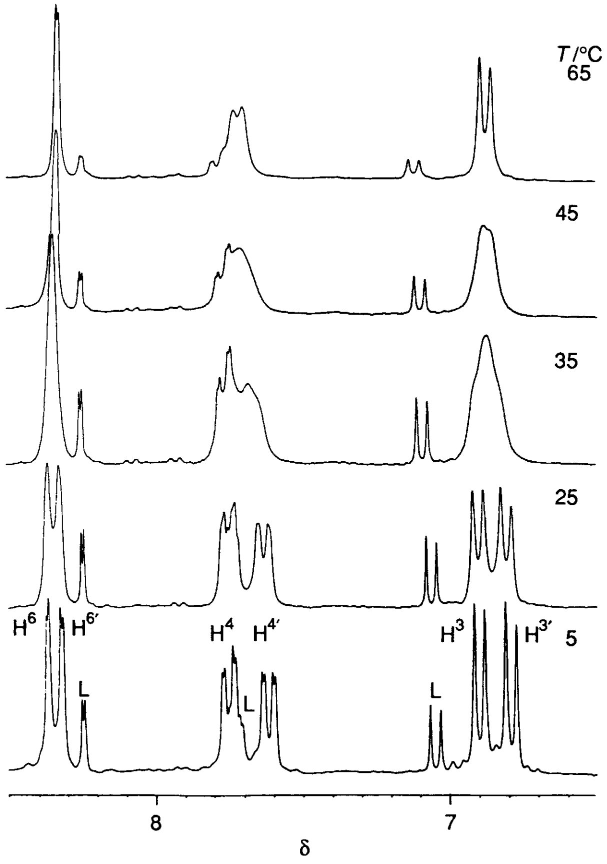


Figure 3. ^1H N.m.r. spectrum (250 MHz, H_2O) of $[InL^1{}_2]^{5-}$ at various temperatures ($[In^{III}]_t$ = 0.020, $[L^1]_t$ = 0.050 mol dm^{-3}, pD 7.4); L = free ligand

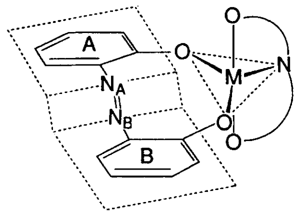


Figure 4. Schematic diagram of a possible transition state or intermediate for the interchange of N_A and N_B (M = In^{III})

trigonal-bipyramidal structure is illustrated in Figure 4. Line-shape analysis[14] in the intermediate-exchange region gave a value for $\Delta G^{\ddagger}$ of $66._5 \pm 2$ kJ mol^{-1} at *ca.* 35 °C. The greater fluxionality of the indium(III) complex, as compared to those of Al^{III} and Ga^{III}, may be associated with the larger size of the indium(III) cation (*cf.* ref. 15).

The $[InL^2{}_2]^{5-}$ complex behaved in a similar manner, although at a given temperature the rate constants for interchange of N_A and N_B were appreciably less (by a factor of *ca.* 3.0 at 50 °C). Values of $\Delta G^{\ddagger}$ obtained from the three coalescence temperatures observed (for H^3,$H^{3'}$, H^6, $H^{6'}$ and Me^4, $Me^{4'}$) were 72.2 at 72, 71.6 at $67._5$, and 70.6 kJ mol^{-1} at 53 °C respectively. The temperature range involved is too small to make a calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ worthwhile, and accordingly we quote $\Delta G^{\ddagger} = 71._5 \pm 2$ kJ mol^{-1} at *ca.* 65 °C. The decreased rate of fluxionality for the $[InL^2{}_2]^{5-}$ complex can be attributed to the CH_3 groups, which are *para* to the N=N bond, increasing the electron density of the nitrogens, and hence the strength of the In–N bond (see below).

For a D_2O solution with $[In^{III}]$ = 0.25, $[H_2L^1]$ = 0.05 mol dm^{-3} and at a pD of 3.6, only resonances from the 1:1 complex were detected. At 27 °C the separate ring resonances were reasonably sharp, showing that intermolecular exchange is appreciably slower than in the 1:2 complex. This implies that the In–N bond is slightly stronger in the 1:1 complex, which might be expected on both steric and electronic grounds.

Asymmetric Ligands.—Since these ligands will adopt an essentially planar configuration, there are three possible isomers for a 1:2 complex (Figure 5). In the AA and BB isomers the two ligands are equivalent, but in the AB isomer they are different. The relative equilibrium concentrations of AA, AB, and BB expected on a purely statistical basis are in the ratio 1:2:1. For a 1:1 complex there are two possible isomers (A and B), in which the metal is bound to N_A or N_B respectively.

The ^1H n.m.r. spectra of the 1:2 complexes of Ga^{III} with four of the asymmetric ligands are given in Figure 6. Only one or two of the ^1H resonances of the ligand are shown. Although a similar pattern was observed with the other ^1H resonances, in most cases appreciable overlap of the peaks occurred. It is clear from Figure 6 that in each case all three isomers are present. Apart from ligand H_2L^{11} [Figure 6(*d*)], where the isomeric distribution is approximately statistical, two resonances of different intensity are observed (from isomers AA and BB), together with two resonances of equal intensity (from AB). Of the two AB resonances, one is closer to the AA and the other to the BB resonance. Accordingly they can be assigned as arising from the A and B ligands in the AB isomer respectively (see Figure 5). The crucial assignment of the AA and BB resonances in Figure 6 is partly based on the assumption that complexation of the gallium(III) ion to one of the azo nitrogens will cause relative deshielding of the Me and H^3 aromatic resonances for the benzene ring attached to the nitrogen (see above). Similar behaviour has also been reported for the complexes of Co^{III} and Pd^{II} with asymmetric 2,2′-dihydroxyazobenzenes.[4–6] In the present work this assumption was unambiguously shown to be correct for the 1:2 complex of Ga^{III} with a modified ligand H_2L^7, in which N_B was 98% enriched in ^{15}N. It is known that, as expected on theoretical grounds, protonation of an *sp*^{2} N, or co-ordination to a metal, produces large upfield shifts in the ^{15}N resonances.[6,16] Figure 7 shows the ^{15}N n.m.r. spectrum of this complex in D_2O. The highest-intensity peak at δ 453.1 p.p.m. can be assigned to the isomer AA. The chemical shift is close to that of the free ligand (448.7 p.p.m.) since it is the adjacent N in both co-ordinated ligands which is bound to the Ga^{III}. The two peaks of equal intensity at δ 453.9 and 356.0 p.p.m. arise from the A and B ligands in the AB isomer, and the weakest peak at δ 353.3 p.p.m. is from the BB isomer, where both ^{15}N atoms in the complex are bound to the Ga^{III}. From the ^{15}N n.m.r. spectra, the ratios 2[AA]/[AB] and [AB]/2[BB] are 2.7 and 2.4:1 respectively, in good agreement with those found from the ^1H n.m.r. spectra (2.7 and 2.2:1, Table 2).

The observed isomer ratios are presented in Table 2. No data are given for ligands H_2L^3 and H_2L^4. When these compounds were dissolved in D_2O rapid deuteriation of $H^{3'}$ occurred at room temperature. In addition, for the 1:2 complexes with Ga^{III}, in both cases the A and B H^3 resonances from the AB isomer overlapped with the AA and BB resonances respectively. It seems that the 3′-Me group in ligands H_2L^5—H_2L^9 not only provides a convenient ^1H n.m.r. probe, but also results in an increased separation of the H^3 resonances in the isomeric complexes.

For an asymmetric 2,2′-dihydroxyazobenzene, if the change in free energy associated with the metal ion moving from one N atom to the adjacent one in the azo group is ΔG kJ mol^{-1} then, in the absence of steric effects, the equilibrium concentrations of the 1:2 isomers AA, AB, and BB should be in the ratio $1:2x:x^2$, where $x = e^{-0.4034\Delta G}$ at 25 °C. It can be seen from the values of 2[AA]/[AB] and [AB]/2[BB], which are given in Table 2 and which should be the same for a particular ligand, that this is only

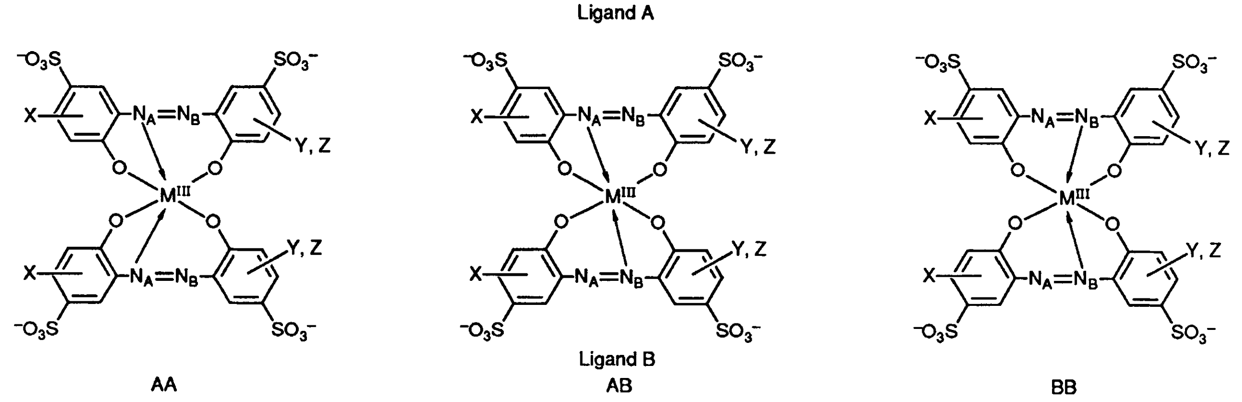


Figure 5. Schematic diagrams for the three isomers of a 1:2 complex with an asymmetric ligand

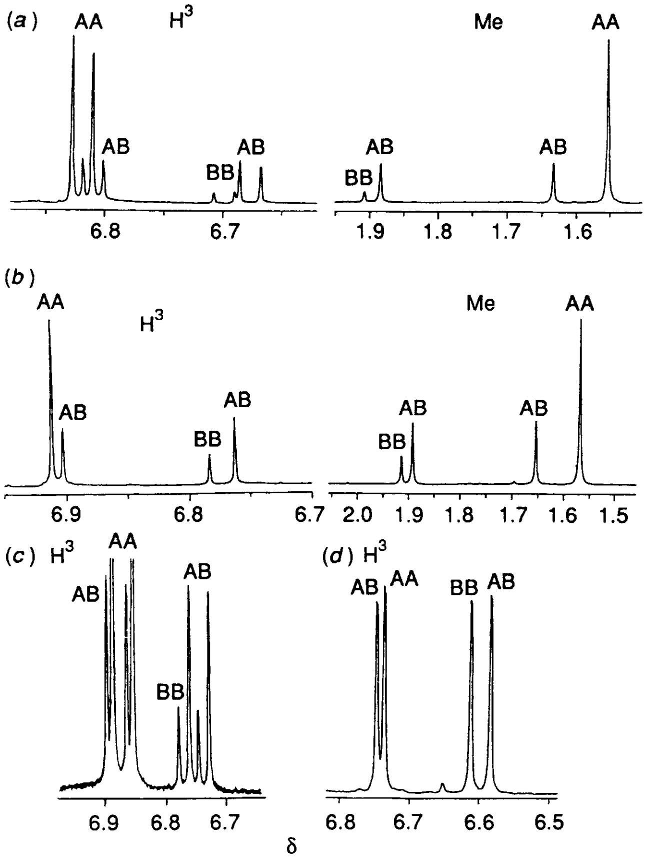


Figure 6. ^1H N.m.r. spectra (D_2O) at 25 °C of (*a*) $[GaL^5{}_2]^{5-}$, H^3, Me; (*b*) $[GaL^9{}_2]^{5-}$, H^3, Me; (*c*) $[GaL^{10}{}_2]^{5-}$, H^3; and (*d*) $[GaL^{11}{}_2]^{5-}$, H^3. $[Ga^{III}]_t$ = 0.025, $[Ligand]_t$ = 0.050 mol dm^{-3}, at pD 6.4 in all cases. Spectra (*a*), (*b*), and (*d*) at 500 MHz, (*c*) at 270 MHz (overlap of resonances at 500 MHz)

Table 2. Isomer ratios for complexes of Al^{III} and Ga^{III} with asymmetric ligands at 25 °C

	Al^{III}			Ga^{III} 1:2 complex[b]	
	1:1 complex[a]	1:2 complex[b]			
Ligand	[A]/[B]	2[AA]/[AB]	[AB]/2[BB]	2[AA]/[AB]	[AB]/2[BB]
H_2L^5	2.4_5	5.6_5	3.7_6	4.7_1	3.8_3
H_2L^6	1.52	3.4_3	3.0_3	2.7_0	2.1_7
H_2L^7	1.46	3.2_7	4.0_0	2.6_8	2.1_7
H_2L^8	1.10	2.2_4	1.85	1.34	1.73
H_2L^9	0.73	1.11	1.07	0.88 (8.4)[c]	0.71
H_2L^{10}				2.0_1	2.5_9
H_2L^{11}				*ca.* 1.0	*ca.* 1.0

[a] $[Al^{III}]_t$ = 0.025, $[Ligand]_t$ = 0.050 mol dm^{-3}, pD 3.4. [b] $[M^{III}]_t$ = 0.025, $[Ligand]_t$ = 0.050 mol dm^{-3}, pD 6.4. [c] At pD ⩾11.

approximately true. Nevertheless, for the 1:2 complexes of Al^{III} and Ga^{III} both ratios follow the same general trend as the substituents on the ligands are altered. For ligands H_2L^5—H_2L^9, with two benzene rings, this trend can be qualitatively understood by considering the changes in the relative electron densities on N_A and N_B caused by substituents *para* to the azo group. Haselbach[17] has measured the pK_a values of a number of *para-* (and *ortho-*)substituted azobenzenes. He has shown that the data can be rationalized on the assumption that protonation takes place on a distinct N atom, and that a Me or OMe substituent *para* to the azo group increases the electron density on the remote N much more than on the adjacent N atom. This can be understood in terms of the resonance structures shown in Figure 8. On this basis, in the isomers of the 1:2 complexes with ligand H_2L^5, the marked preference of Al^{III} and Ga^{III} for co-ordination to N_A can be largely attributed to the presence of the 4′-OH group, which will give N_A a negative charge relative to N_B.

For the 1:2 complexes with ligands H_2L^5, H_2L^8, and H_2L^9, where the 4-substituent is (H), Me, and OMe respectively, there is a reasonable correlation between the values of $\log_{10}$ (2[AA]/[BB]) and $\log_{10}$ ([AB]/2[BB]) and the Hammett σ_p parameters[18] for the substituent (*cf.* also the result below for O^- on the 4′-position). This relationship does not, however, apply to ligands H_2L^6 and H_2L^7, where the observed ratios are *less* than with H_2L^5. It seems likely that, with F and Cl, the resonance effect (Figure 8) outweighs the inductive effect.

Ligand H_2L^{10} contains identically substituted benzene and naphthalene rings. In the 1:2 complex with Ga^{III}, co-ordination to the N attached to the benzene ring is preferred, as expected since the azo group should conjugate more with the naphthalene than with the benzene ring, as a result of the greater delocalization of charge in the former.[19] The presence of a 4-Me group on the benzene ring in ligand H_2L^{11} compensates for this, and an approximately statistical distribution of the isomers is found (Figure 6 and Table 2).

For the 1:1 complexes with Al^{III} (Table 2), the ratios [A]/[B] follow the same trend as the (statistically corrected) ratios for the 2:1 complexes but the actual values are lower by a factor of *ca.* 2.

Ligands H_2L^3—H_2L^9 contain a 4′-OH group, since this enabled them to be easily prepared by the diazonium coupling reaction. Accordingly, the 1:2 complexes of these ligands have

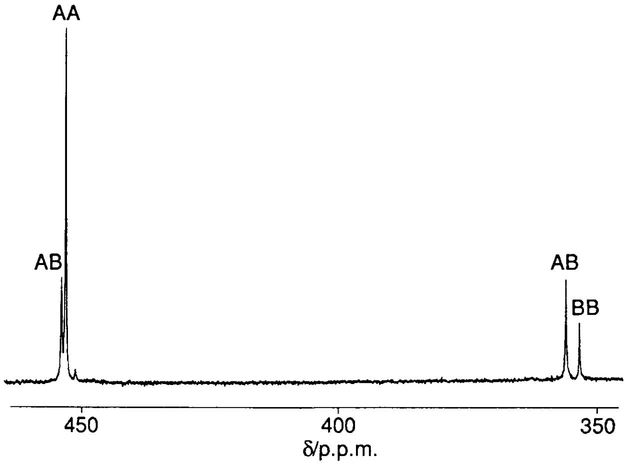
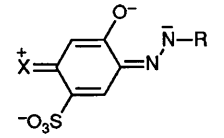


Figure 7. ^{15}N N.m.r. spectrum (50.7 MHz) of $[GaL^7{}_2]^{5-}$ in D_2O ($[Ga^{III}]_t$ = 0.125, $[L^7]_t$ = 0.25 mol dm^{-3}, pD 6.4) at 25 °C; N_B of the ligand was enriched with ^{15}N (98%)



X = O$^-$, OMe, OH, Me, F, or Cl; R = aryl

Figure 8. Resonance structure showing the effect of certain *para* substituents on the electron density on the remote nitrogen of the azo group

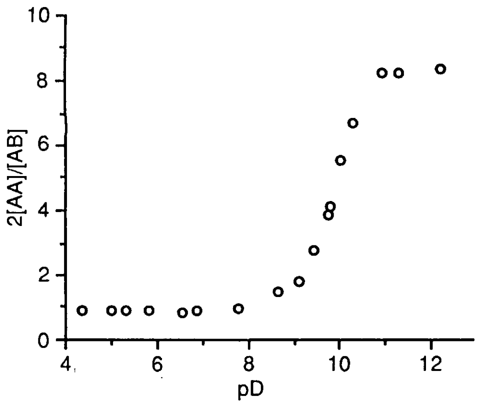


Figure 9. A plot of the isomer ratio 2[AA]/[BB] at 25 °C against pD for $[GaL^9{}_2]^{5-}$ ($[Ga^{III}]_t$ = 0.025, $[L^9]_t$ = 0.05 mol dm^{-3})

two potentially ionizable protons (or deuterons in D_2O). Figure 9 shows a plot of the ratio 2[AA]/[AB] against pD for the $[GaL^9{}_2]^{5-}$ complex. The very considerable increase in this ratio between pD *ca.* 7 and *ca.* 11 can be attributed to the loss of one or both of these deuterons. A similar increase was observed for the ratio [AB]/2[BB], but accurate values could not be obtained because of peak overlap in these alkaline solutions. A pD titration of the complex with concentrated aqueous NaOH showed that approximately two deuterons were lost over this pD range. More detailed information could be obtained from the chemical shifts of the 4′-Me protons as a function of pD for the AA and AB isomers (Figure 10). The data for the A and B ligands of the AB isomer can be fitted quite well by assuming a single p*K* in each case ($pK_A = 8.5_5$, $pK_B = 10.0_9$).[20] These values presumably represent, to a reasonable approximation, the *microscopic* constants for ionization of the OD deuterons from the A and B ligands respectively. The fact that pK_A is considerably less than pK_B can be qualitatively understood, since the stability of the resonance structure shown in Figure 8 will be markedly increased through withdrawal of electron density from N_B by the gallium(III) ion. As expected, two p*K* values (pK_1 = *ca.* 8.4 and pK_2 = *ca.* 9.5) are required to give a reasonable fit for the data from the AA isomer (Figure 10).

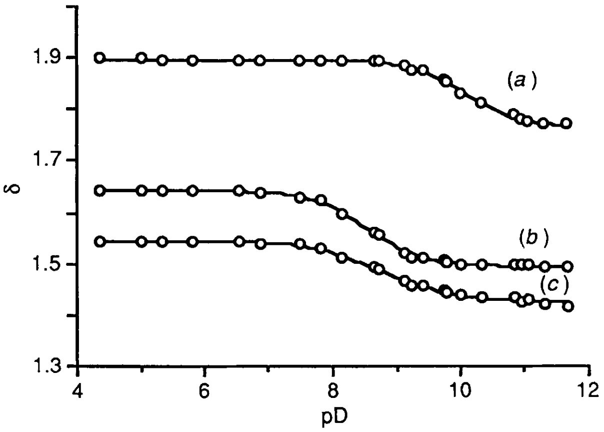


Figure 10. Plots of the 3′-Me ^{1}H n.m.r. chemical shifts against pD for the isomers of $[GaL^9{}_2]^{5-}$; (*a*) B ligand of AB; (*b*) A ligand of AB; and (*c*) AA. The curves were calculated using the procedure given in ref. 20, with the following parameters: (*a*) δ_{BH} 1.898, δ_{B^-} 1.767, pK_B = 10.09; (*b*) δ_{AH} 1.643, δ_{A^-} 1.493, pK_A = 8.55; (*c*) δ_{AAH_2} 1.544, δ_{AAH} 1.474, δ_{AA} 1.427, pK_1 = 8.36, pK_2 = 9.48

In principle it should be possible, using this information on p*K* values, to calculate a 'theoretical' curve for the results plotted in Figure 9. However, this was not attempted in view of the uncertainties involved. Nevertheless, it is clear that the isomer ratio below pD *ca.* 7 (average value 0.88) is for the complex $[GaL^9{}_2]^{5-}$, whilst that above pD *ca.* 11 (average 8.4) corresponds to a complex in which both 4′-OD deuterons have been lost. This almost 10-fold increase in the isomer ratio 2[AA]/[AB] is not surprising in view of the very powerful electron-donating nature of O^- as an aromatic substituent.[18,21]

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References

1 R. Price, in 'The Chemistry of Synthetic Dyes,' ed. K. Venkataraman, Academic Press, New York, 1970, vol. 3, p. 249.
2 E. Wanninen, in 'Indicators,' ed. E. Bishop, Pergamon, Oxford, 1972, p. 231; F. D. Snell, 'Photometric and Fluorometric Methods of Analysis, Metals, Parts I and II,' Wiley, New York, 1978.
3 L. D. Durfee, J. E. Mill, P. E. Fanwick, and L. P. Rothwell, *Organometallics*, 1990, **9**, 75 and refs. therein.
4 G. Schetty and E. Steiner, *Helv. Chim. Acta*, 1972, **55**, 1509; 1974, **57**, 2149; E. Steiner, C. Mayer, and G. Schetty, *ibid.*, 1976, **59**, 364.
5 P. S. Pregosin and E. Steiner, *Helv. Chim. Acta*, 1979, **62**, 62.
6 P. S. Pregosin and E. Steiner, *Helv. Chim. Acta*, 1976, **59**, 376.
7 H. H. Hodgson and A. Kershaw, *J. Chem. Soc.*, 1928, 2073.
8 F. Henrich and H. Birkner, *Ber. Dtsch. Chem. Ges.*, 1913, **46**, 3380.
9 O. Süs, *Liebig's Ann. Chem.*, 1944, **556**, 65.
10 J. Turner, *J. Soc. Chem. Ind.*, 1915, **34**, 585.
11 G. H. Jeffrey, J. Basset, J. Mendham, and R. C. Denney, 'Vogels' Textbook of Quantitative Chemical Analysis,' 5th edn., Longman, Harlow, 1989.
12 R. G. Bates, 'Determination of pH, Theory and Practice,' Wiley, New York, 1964, p. 219.
13 D. F. Evans and D. A. Jakubovic, *Polyhedron*, 1988, **7**, 2723.

14 G. Stevenson and G. Binsch, Quantum Chemistry Program Exchange, Program No. 485 (DNMR 3H), Indiana State University, Indiana.

15 D. F. Evans and D. A. Jakubovic, *Polyhedron*, 1988, **7**, 1881 and refs. therein.

16 G. C. Levy and R. L. Lichter, 'Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy,' Wiley, New York, 1979.

17 E. Haselbach, *Helv. Chim. Acta*, 1970, **53**, 1526.

18 J. March, 'Advanced Organic Chemistry,' 3rd edn., Wiley, New York, 1985, p. 244.

19 Ref. 18, p. 460.

20 D. F. Evans and G. K. Turner, *J. Chem. Soc., Dalton Trans.*, 1975, 1238.

21 J. Hine, *J. Am. Chem. Soc.*, 1960, **82**, 4877.

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