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Aluminium-27 Solid-State NMR Study of Aluminium Coordination Complexes of Alizarin

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The structures of complexes obtained by the reaction of alizarin ($C_{14}H_8O_4$) and Al^{3+} in basic media depend upon the reaction solvent and the nature of the base. With aqueous or methanolic solutions of sodium hydroxide a binuclear complex $[Al_2(\mu\text{-}OH)_2(C_{14}H_6O_4)_4(Na)_4(H_2O)_4]$ was obtained, which is stable as the tetrahydrate and is observed even in the gas phase by electrospray mass spectrometry. With potassium hydroxide the monohydrate form is obtained. These two products are distinguishable by ^{27}Al NMR in the solid state by means of their chemical shifts (+23.1 and 0.0 ppm) and their linewidths $\Delta\nu_{1/2}$ (1200 and 4000 Hz). The chemical shifts of these binuclear complexes or similar derivatives are discussed in relation to possible chelation of the four molecules of water with alizarinate entities according to the bulk of the cation. The results are illustrated by two types of structure, named 'closed structure' (with strongly chelated H_2O molecules and dibenzene sandwich Na^+) and 'open structure'.

KEY WORDS ^{27}Al solid-state NMR; alizarin; coordination compound; dyes

INTRODUCTION

Being interested in the problem of the degradation mechanism of natural dyes used in ancient tapestries, we began a study with alizarin (**1**) (Scheme 1). Alizarin is the main component of madder, which has been used with aluminium as a mordant to obtain red colours on cotton, wool, silk, etc. We are concerned with two aspects: (i) structure determination of the complex formed with the three entities alizarin, aluminium cation (Al^{3+}) and the fibres and (ii) a study of its stability under various influences (sunlight, moisture, etc.). First, we synthesized in various solvents some coordination complexes obtained with alizarin or the substituted alizarins **3** or **4** (Scheme 2) and aluminium in basic media in the absence of fabric.

These alumino complexes give coloured amorphous lacquers which do not crystallize under normal conditions. We have studied their structure by NMR (high-resolution ^1H and ^{13}C in DMSO-d_6 solution and ^{27}Al in the solid state) and by electrospray mass spectrometry (ESMS).[1–3] Another preparation was described by Kiel and Heertjes[4,5] in 1963. They undertook a structural study and obtained a good microanalysis for mononuclear $[AlOH(C_{14}H_6O_4)_2Ca(H_2O)_3]$ in the case of a complex obtained in aqueous solution with Al^{3+} chelated in the β-ketol position of alizarin (Fig. 1). Recently, Wunderlich and Bergerhoff[6] obtained a crystallized binuclear complex in DMF. They demonstrated by an X-ray study[7] that this complex contains four metal atoms, two Al^{3+} and two Ca^{2+}, chelated in the α-diol or β-cetol position of alizarin, respectively. ESMS indicated that complexes obtained in water or methanol have a binuclear structure that is completely different.

Aluminium-27 NMR in the solid state[8] is generally used for aluminosilicates,[9] zeolites[10,11] and intercalated species such as hectorite.[12] Its application in the case of coordination complexes remains uncommon.[13,14] In this paper, we show that ^{27}Al NMR in the solid state is a good tool for distinguishing, among these binuclear coordination complexes synthesized in water or methanol, two families depending on the counterion (Na^+, K^+, Ca^{2+}, etc.), which we name 'open structure' or 'closed structure.' The complex obtained by Kiel and Heertjes[4,5] is in fact a dimer structure of the formula they proposed and is a member of the family of closed structure binuclear complexes.

RESULTS AND DISCUSSION

The *m*/*z* values observed in ESMS show that our binuclear species consist of a tetraanion skeleton formed around two Al^{3+} ions linked by two hydroxyl bridges.[15] To date, only six examples of Al(III) complexes with an $[Al_2(\mu\text{-}OH)_2]^{4+}$ core have been structurally characterized.[16–21] High-resolution ^{27}Al NMR spectra were obtained in three cases: I, $[Al_2(\mu\text{-}OH)_2(H_2O)_8]\cdot(SO_4)_2\cdot 2H_2O$ (δ^{27} Al = 3.5 ppm, $\Delta\nu_{1/2} = 700$ Hz in aqueous solution[22]); II, $[Al_2(\mu\text{-}OH)_2(en)_2(OCH(CF_3)_2)_4]$ (δ^{27} Al = 7.0 ppm, $\Delta\nu_{1/2} =$ 200 Hz in C_6D_6 solution[17]); and III, $[Al_2(\mu\text{-}OH)_2(hbo)_4]\cdot 4CH_3OH\cdot H_2O$ (δ^{27} Al = 5.0 ppm, $\Delta\nu_{1/2} = 2000$ Hz in $CDCl_3$ solution[19]). The eight water

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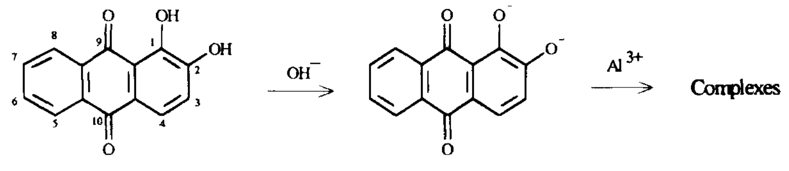
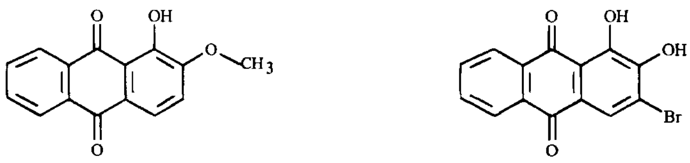


1 2

Scheme 1

molecules in I or the four ligands in II and III are substituted by four alizarinate **2** in our complexes (Scheme 1 and Fig. 2). Depending on the nature of the cation (Na^+, K^+, Ca^{2+}, Ba^{2+}) and the conditions of the drying (cf. Experimental section), they are surrounded by a varying number (*i*, *j*) of water molecules $[Al_2(\mu\text{-}OH)_2(C_{14}H_6O_4)_4(H_2O)_i](H_2O)_j^{4-}$. Thermogravimetric analysis and ^{1}H NMR in DMSO solution (we calculated the loss of mass between sample and reference, which was related to the integration of H_2O NMR signals, at different stages: A, B, C and D) allowed us to determine the different hydration states (*i*, *j*) of each complex (Fig. 3). By comparison of the results obtained by variation of the temperature gradient, we are able to distinguish two families of water molecules (*i* and *j*). One of these families (*i*) is characterized by tightly bound water molecules. Complexes **5**, **6**, **7** and **8** (Table 1) contain four strongly bound H_2O molecules, complexes **9** and **11** contain only one and complex **10** contains three water molecules of this kind. The other molecules (*j*) are characterized as containing more loosely bound water molecules (cf. Table 1). The high-resolution ^{1}H and ^{13}C NMR spectra are very simple because the organic ligands are equivalent (cf. Experimental section), except for the binuclear alizarin–Ba^{2+} trihydrate complex (**10**), which shows two different ligand groups.

^{27}Al NMR in the solid state is a good tool for the determination of the aluminium coordination number in complexes. It is well known that ^{27}Al NMR in the solid state shows a signal between −10 and +20 ppm for coordination number six and between +55 and +85 ppm for coordination number four. Some rare examples of five-coordinate Al are known, with signals



3 4

Scheme 2

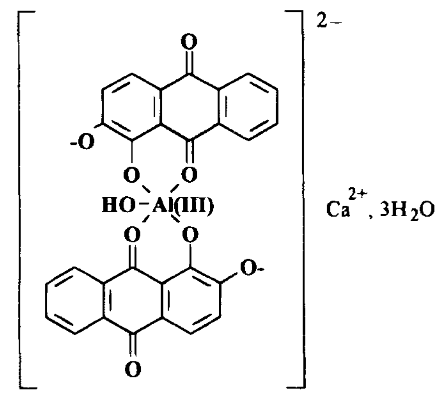


Figure 1. Kiel and Heertjes's model.[4,5]

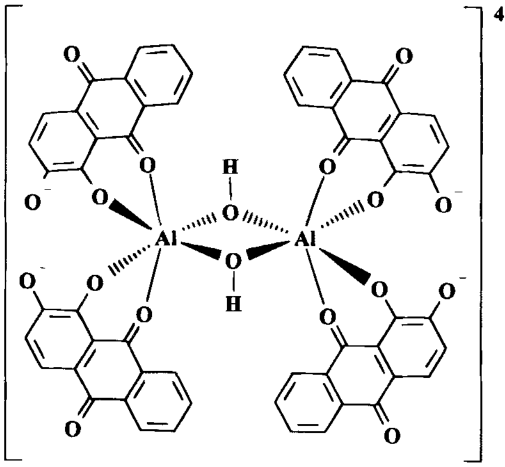


Figure 2. $[Al_2(\mu\text{-}OH)_2(C_{14}H_6O_4)_4]^{4-}$ core of the binuclear complex.

Table 1. ^{27}Al NMR in the solid state of the binuclear complexes and model compounds

Compounds	Entry	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)
$[Al_2(\mu\text{-}OH)_2Na_2(C_{14}H_6O_4)_4(H_2O)_4](H_2O)_2(Na)_2$	5[a]	23.1	1200
$[Al_2(\mu\text{-}OH)_2Na_2(C_{14}H_5BrO_4)_4(H_2O)_4](H_2O)_2(Na)_2$	6	22.3	1000
$[Al_2(\mu\text{-}OH)_2Ca_2(C_{14}H_6O_4)_4(H_2O)_4](H_2O)_2$	7	24.7	1000
$[Al_2(\mu\text{-}OH)_2Ca_2(C_{14}H_5BrO_4)_4(H_2O)_4](H_2O)_2$	8	24.2	1250
$[Al_2(\mu\text{-}OH)_2(C_{14}H_6O_4)_4(H_2O)](H_2O)_6(K)_4$	9	0.0	4000
$[Al_2(\mu\text{-}OH)_2(C_{14}H_6O_4)_4(H_2O)_3](H_2O)_3(Ba)_2$	10	−1.9	3500
$[Al_2(\mu\text{-}OH)_2(C_{14}H_6O_4CH_3)_4(H_2O)](H_2O)_6$	11	0.6	2700
$Al(acac)_3$	12	−5.2	700
$[Al_2O_2H_2(C_{14}H_6O_4)_4Ca_2(C_3H_7NO)_4(H_2O)_2](C_3H_7NO)_3(H_2O)_3$	13[b]	25.8	980

[a] The tetrahydrate and dodecahydrate analogues show similar chemical shifts (23.4 and 22.0 ppm) and the same linewidth.

[b] Synthesized following the first procedure in Ref. 6.

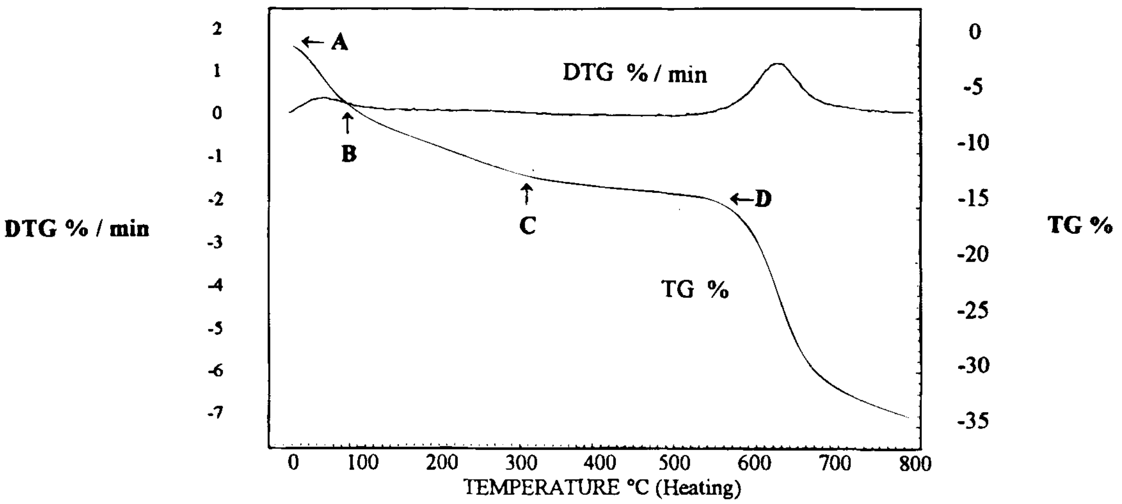


Figure 3. Thermogravimetric curves for the binuclear complex **5** under N_2 (200 ml min^{-1}) TG (%) = loss of mass between sample and reference; DTG (% min^{-1}) = TG derived (i, j) water molecules in complex **5** at different stages: A $(i = 4, j = 2)$; B $(i = 4, j = 0)$; C $(i = 0, j = 0)$ and D $(i = 0, j = 0)$.

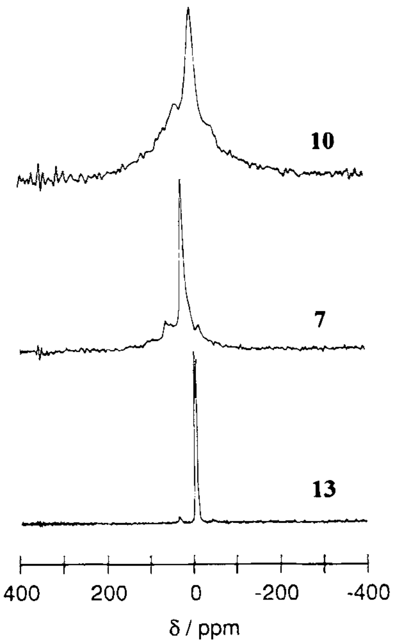


Figure 4. ^{27}Al NMR spectra of an 'open structure' model complex (**10**), a 'closed structure' complex (**7**) and a standard octahedral complex (**13**).

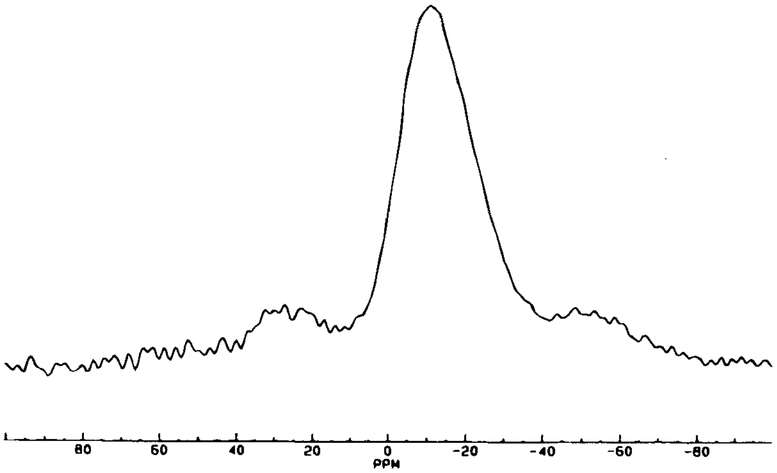


Figure 5. ^{23}Na solid-state NMR spectrum of the binuclear complex **5** ($6H_2O$). $\delta^{23}Na \approx -11$ ppm, $\Delta\nu_{1/2} = 2400$ Hz.

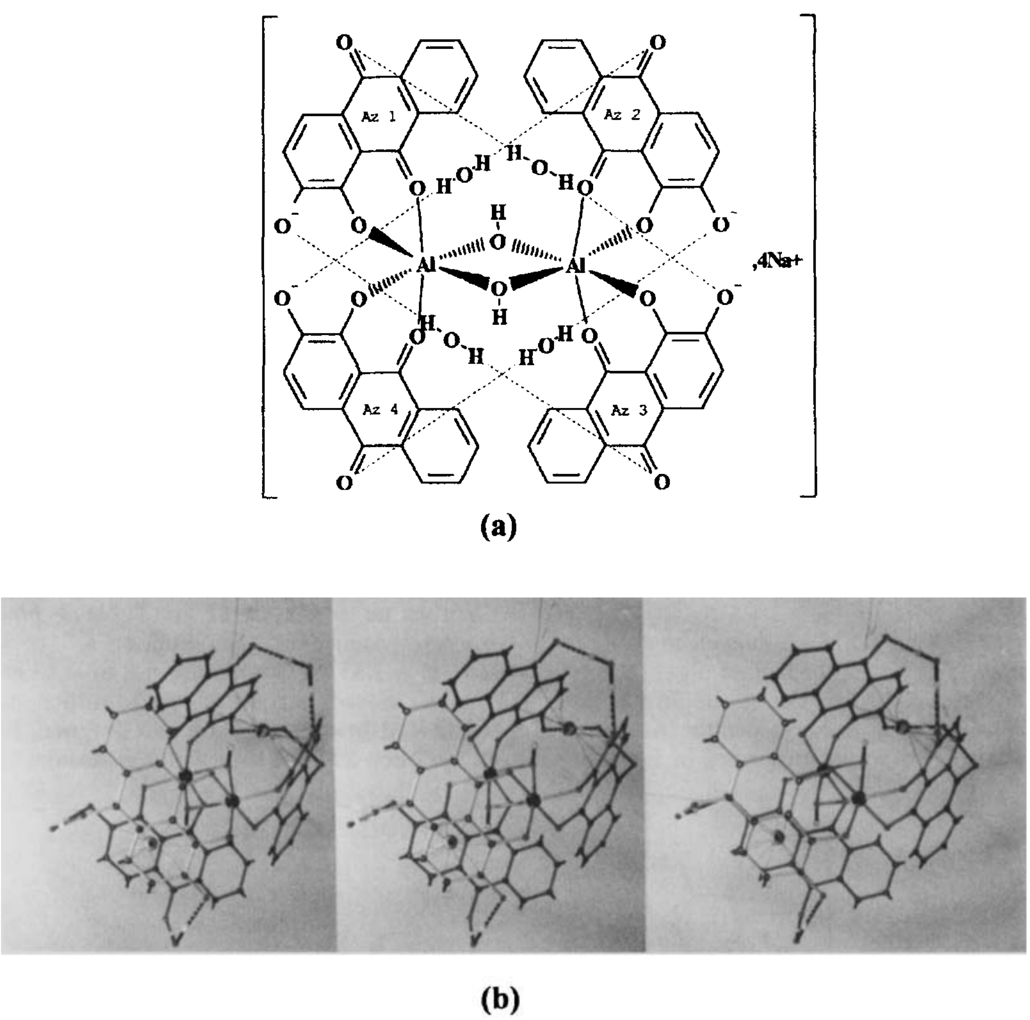
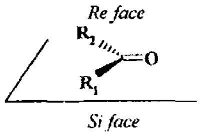


Figure 6. (a) Structure of the tetrahydrate complex **5** and (b) a stereoscopic view of a molecular model with the two internal sodium ions. The ligands Az2 and Az4 are viewed by their *Si* faces and Az1 and Az3 viewed by their *Re* faces. By closing the structures all *Re* faces come face-to-face. In the enantiomeric form the phenate groups linking Az2 and Az3 to Al, and also the two linking Az1 and Az4 to Al, are exchanged. Now closing the structures makes the *Si* faces come face-to-face. The notation of *Re* and *Si* faces is often used in organic stereochemistry with the following significance:



where R_1 is prior to R_2.[30]

near +35 ppm.[23] The chemical shifts of the complexes we obtained in ethanol or *tert*-butanol are found at negative values near −20 ppm and will be discussed in a further paper. Table 1 reports the chemical shifts δ of the binuclear alizarin complexes and their linewidths $\Delta\nu_{1/2}$ (Fig. 4). We have also experimented on and reported the model compounds $Al(acac)_3$ (data in conformity with the literature[24]) and $[Al_2O_2H_2(C_{14}H_6O_4)_4\ Ca_2(C_3H_7NO)_4(H_2O)_2]\ (C_3H_7NO)_3(H_2O)_3$ (**13**[7]). The complex $[Al(H_2O)_6]^{3+}$ is used as a reference [δ^{27}Al = 0 ppm for $Al(NO_3)_3$ in aqueous solution].

In the *binuclear family* (entries **5**–**11**, Table 1) two types of complexes are observed, depending on the bulkiness of the counterion. For the compounds **9** (0.0 ppm), **10** (−1.9 ppm) and **11** (0.6 ppm), the chemical shifts are in conformity with the hexacoordinated models (Table 1). The binuclear constitutional tetrahydrate complexes with Na^+ (**5** or **6**) and Ca^{2+} (**7** or **8**) give ^{27}Al signals which are too deshielded for octahedral standard structures (δ = 22–25 ppm). ESMS shows that in these complexes the four H_2O molecules and at least two of the Na^+ or two Ca^{2+} cations are very strongly bound to the tetraanion even in the gas phase. However, the ^{23}Na NMR spectrum of **5** in the solid state shows only one signal at −7 to −13 ppm according to the hydrate form (Fig 5; the chemical shift reference is aqueous NaCl solution). The ^{23}Na chemical shift range is too short to distinguish two types of Na^+ among the four in complex **5** as was the case using ESMS. However, the observed chemical shifts in the ^{23}Na NMR spectra show that the Na^+ cations have a specific interaction with the tetraanion in the lacquer.

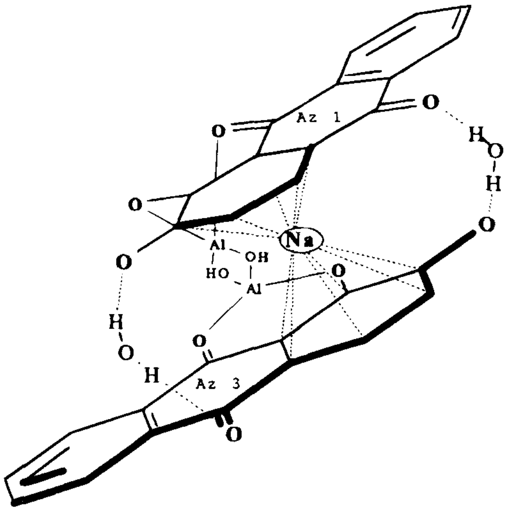
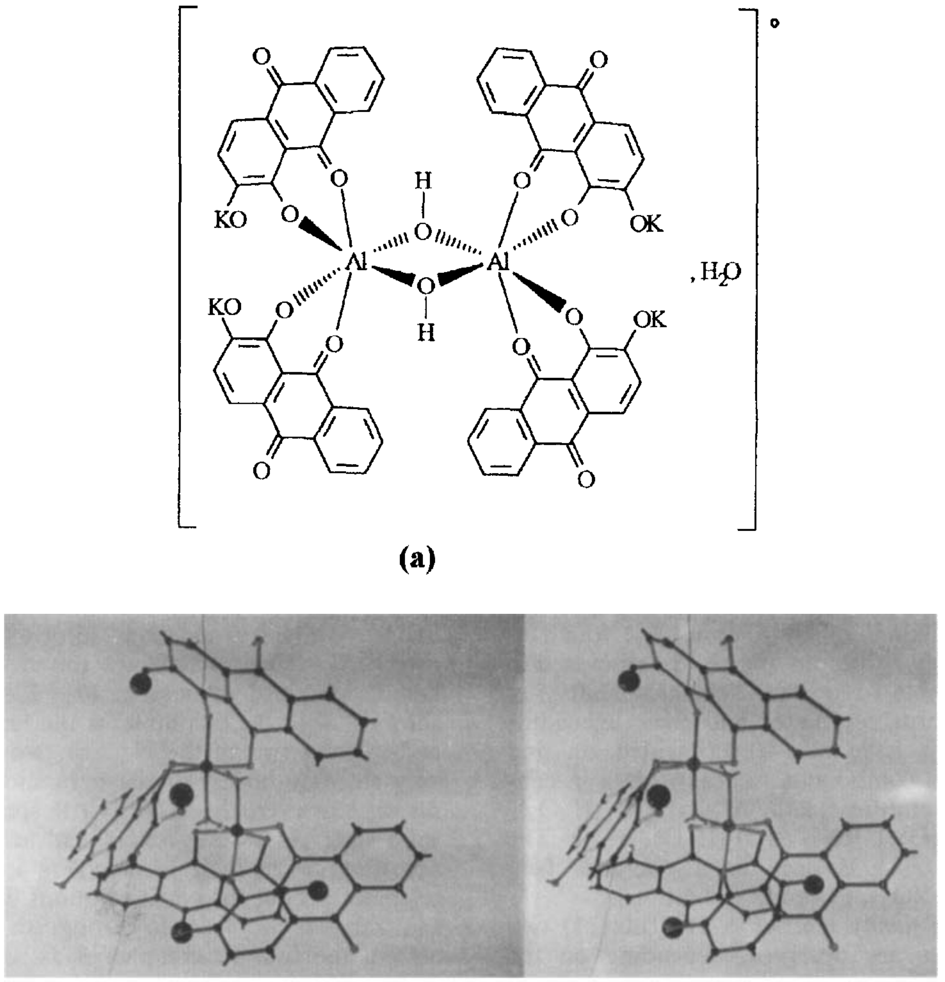


Figure 7. Structure of the tetrahydrate complex; partial perspective view of half of the molecule with one internal sodium.

We name entries **5**–**8** in Table 1 *binuclear 'closed structure' complexes.* The four alizarinate ligands are probably bound by their eight free O^- to the four H_2O molecules as shown in Fig. 6. Alizarin groups Az1 and Az3 are folded in with two water molecules in front of the complex and the groups Az2 and Az4 are folded in with the other two water molecules at the rear of the complex. Hence it is always the same *Re* or *Si* faces (Fig. 6) of the alizarin entities which are opposite each other, making a sandwich structure with two benzenes inside of which two of the four Na^+ or two Ca^{2+} cations are probably confined (Fig. 7, dibenzene sandwich in closed structure **5** complex). The ionic radii of *ca* 0.95 and 0.99 Å of Na^+ and Ca^{2+} fit nicely into a benzene hexagon of 2.4 Å diameter, which therefore supports the formation of $(C_6H_6)_2Na$ sandwich subunits.[25–27] In the binuclear closed structure complexes, shutting the ligands leads to a stretching and bending of the central square ring and introduces a lot of strain. This strain mainly reflects the steric bulk of the ligands. Deformation of the four O—Al bonds in the $[Al_2(\mu\text{-}OH)_2]^{4+}$ core is probably responsible for the decrease in the apparent coordination number of Al in the closed complex **4**, leading to an atypical chemical shift for ^{27}Al near 24 ppm.

We name entries **9**–**11** in Table 1 *binuclear 'open structure' complexes.* The bulkier K^+ ($r = 1.33$ Å) or Ba^{2+} ($r = 1.35$ Å) cations are not able to enter the alizarinate 'closed structure' and rather than having Al—O—Al bridges that are too strained, the structures remain open and the four water molecules are no longer



(a)

(b)

Figure 8. (a) Structure of the monohydrate complex **9** and (b) a stereoscopic view of the molecular model.

necessary (Fig. 8). In this case, the coordination number six gives standard chemical shifts near zero and probably standard O—Al bond lengths near 1.86 Å, as in $[Al_2(\mu\text{-}OH)_2]^{4+}$ core complexes.[16–22] In the case of Ba^{2+} the stable complex **10** is a trihydrate: there are probably two alizarinates closed by two H_2O molecules, the other two ligands remaining open. This particular structure takes into account the observed splitting of the signals for the alizarin groups in the ^{1}H and the ^{13}C NMR spectra in solution. Complex **11** is a neutral molecule that cannot be strongly bound to H_2O. It is not surprising that it remains open.

The linewidths of ^{27}Al NMR solid-state spectra (Fig. 4) of the complexes with K^+ (**9**) or Ba^{2+} (**10**) (3500 and 4000 Hz) are greater than with Na^+ or Ca^{2+} (entries **5**–**8**, Table 1) (1000–1250 Hz), which is related to the rigidity and homogeneity of the surrounding symmetry of the latter complexes having the 'closed structures.' In fact, the linewidths in NMR of ^{27}Al in the solid state depend mostly on the geometry around the aluminium nucleus; the more rigid the complex, the narrower is the linewidth. In amorphous binuclear closed complexes (entries **5**–**8**, Table 1) the symmetry is strictly defined and regular because of the strong cohesion forces so the linewidth is narrow (1000–1250 Hz). However, in amorphous binuclear open complexes (entries **9**–**11**, Table 1) the open structure can fluctuate from one complex to another, and even with a molecular model it is difficult to choose the most probable conformation. Therefore, the linewidth is larger (3500 and 4000 Hz). These results are consistent with the proposed 'open' and 'closed structures.'

CONCLUSION

NMR of ^{27}Al in the solid state allows us to show the existence of two distinct families in binuclear aluminium complexes synthesized in water or methanol with alizarin. The first, which we call 'open structures,' shows typical values of the chemical shift for hexacoordinated aluminium near 0 ppm. In the 'closed structure' family, there is a lot of strain around the aluminium atoms. Such strain results mainly from enclosing Na^+ cations, for example, into dibenzene sandwiches. In such cases, we observe borderline chemical shifts around 22–25 ppm, which extends the chemical shift range of hexacoordinated aluminium.

Regarding our initial purpose, the proposed 'closed structure' for Na^+ or Ca^{2+} complexes is interesting. Inspection of molecular models shows that the two H_2O molecules of each dibenzene sandwich may be replaced by a cellobiose entity representing a unit of the cellulose fibre (Fig. 9). This possibility could provide a good explanation of the strong fixation of this dye on cotton fabric and is different from the earlier hypothesis.[28]

EXPERIMENTAL

NMR spectroscopy

^{27}Al and ^{23}Na solid state magic angle spinning NMR spectra were obtained at 104.2 MHz for ^{27}Al and 105.8 MHz for ^{23}Na on a Bruker MSL-400 multinuclear spectrometer equipped with a double-bearing probehead free of background aluminium signal. Single-pulse sequences were applied with 1 μs pulse duration (9° flip angle), 6 μs acquisition delay and 1 s recycle delay. The spinning rate of the standard 7 mm zirconia rotor was 4 kHz. The usual sign convention of high-frequency shifts being positive was used.

Proton NMR spectra were recorded on Bruker AM-500 and WM-250 spectrometers. The chemical shifts of the proton spectra were measured by taking the dimethyl sulphoxide signal at $\delta = 2.5$ ppm (DMSO-d_6 solution).

Thermogravimetry

TG/DTA measurements were carried out on a Seiko TG/DTA 220 thermogravimetric/differential thermal

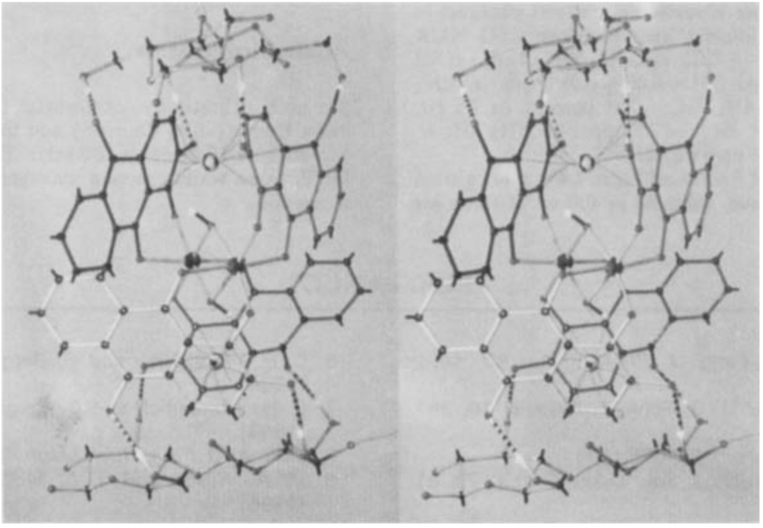


Figure 9. Stereoscopic view of an idealized closed structure (entries **5**–**8** in Table 1) molecular model with two cellobiose entities.

analyser under nitrogen (200 ml min^{-1}) with a temperature gradient of 5 °C min^{-1} between 25 and 800 °C.

Synthesis

We synthesized alumino complexes with alizarin (**1**) and with two derivatives, 1-hydroxy-2-methoxyanthraquinone (**3**) and 3-bromoalizarin (**4**).[29] Experiments were carried out with NaOH, KOH, $Ca(OH)_2$ or $Ba(OH)_2$ as bases and in H_2O, MeOH, EtOH and *t*-BuOH as solvents. Aluminium was introduced as its sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$, except in the case of $Ba(OH)_2$, for which we used $AlCl_3 \cdot 6H_2O$. Different degrees of condensation in Al are obtained according to the solvent used in the synthesis. Binuclear complexes are formed in water or methanol. In ethanol or *tert*-butanol, other degrees of condensation are observed. In basic media the organic ligand is an alizarinate dianion (**2**) (or a monoanion in the case of **3**).

Closed structure binuclear complexes with NaOH (complexes 5 and 6). For complex **5** a solution of 5 g of alizarin, 2.084 g of sodium hydroxide and 3.469 g of aluminium sulphate [$Al_2(SO_4)_3 \cdot 18H_2O$] in 400 ml of water (or methanol) is heated at reflux for 1 h with vigorous magnetic stirring. The synthesis gives a red lacquer containing Na_2SO_4. After filtration of the hot solution, its volume is reduced to 80 ml by evaporation and then centrifuged at 10000 rev min^{-1} for 30 min. The solid part is dispersed in 100 ml of water (or methanol) and then ultrafiltered through a 1000 Da membrane. The solid lacquer obtained under these conditions gives four different hydration forms depending on the drying procedures, as is easily determined by ^1H NMR. When heated at 110 °C, it gives the stable hydrate with $12H_2O$. After azeotropic distillation with benzene we obtained the hexahydrate and by heating at 250 °C (0.2 mmHg) the tetrahydrate form in quantitative yields. The drying procedures were the same for all the complexes. In the case of these three hydrate complexes we always observed two OH signals by ^1H NMR in DMSO-d_6 (99.96%), attributed to H_2O and to the Al—OH—Al bridges. ^1H NMR (DMSO solution): $\delta H_2O = 3.34 \pm 0.02$ ppm (s, 24H, 12H or 8H according to the complex), δAl—OH = 3.12 ± 0.06 ppm (s, 2H), $\delta H_3 = 6.26$ ppm (d, 8.1 Hz, 4H) and $\delta H_4 = 7.37$ ppm (d, 8.1 Hz, 4H), four equivalent AB systems, $\delta H_{6,7} = 7.73$ ppm (m, 8H), $\delta H_5 = 8.03$ ppm (m, 4H) and $\delta H_8 = 8.36$ ppm (m, 4H).

The same procedure with a solution of 5 g of 3-bromoalizarin, 1.568 g of sodium hydroxide and 2.61 g of aluminium sulphate in 400 ml of water (or methanol) gave the complex **6**. ^1H NMR (DMSO solution): $\delta H_2O = 3.34 \pm 0.02$ ppm (s, 24H or 12H or 8H according to the complex), δAl—OH = 3.51 ± 0.06 ppm (s, 2H), $\delta H_4 = 7.49$ ppm (s, 4H), $\delta H_{6,7} = 7.73$ ppm (m, 8H), $\delta H_5 = 8.00$ ppm (m, 4H) and $\delta H_8 = 8.37$ ppm (m, 4H).

Closed structure binuclear complexes with $Ca(OH)_2$ (complexes 7 and 8). For complex **7**, a solution of 5 g of alizarin, 1.931 g of calcium hydroxide and 3.469 g of aluminium sulphate in 400 ml of water (or methanol) was heated under reflux for 1 h with vigorous magnetic stirring. After filtration of the hot solution, the solid part was washed with hot water. The solid lacquer is insoluble and was obtained in quantitative yield as its three different hydration forms. ^1H NMR (DMSO solution): $\delta H_2O = 3.34 \pm 0.02$ ppm (s, 24H, 12H or 8H according to the complex), δAl-OH = 6.06 ± 0.06 ppm (s, 2H), $\delta H_3 = 6.48$ ppm (d, *ca* 7.5 Hz, 4H), $\delta H_4 = 7.51$ ppm (d, *ca* 7.5 Hz, 4H), four equivalent AB systems, $\delta H_{6,7} = 7.82$ ppm (m, 8H), $\delta H_5 = 8.09$ ppm (m, 4H) and $\delta H_8 = 8.48$ ppm (m, 4H).

By the same procedure, 5 g of 3-bromoalizarin, 1.452 g of calcium hydroxide and 2.61 g of aluminium sulphate in 400 ml of water (or methanol) gave the solid laquer **8**. ^1H NMR (DMSO solution): $\delta H_2O = 3.34 \pm 0.02$ ppm (s, 24H, 12H or 8H according to the complex). δAl-OH = 6.42 ± 0.06 ppm (s, 2H), $\delta H_4 = 7.65$ ppm (s, 4H), $\delta H_{6,7} = 7.81$ ppm (m, 8H), $\delta H_5 = 8.07$ ppm (m, 4H) and $\delta H_8 = 8.47$ ppm (m, 4H).

Open structure binuclear complexes with KOH (complex 9). A solution of 5 g of alizarin, 2.915 g of potassium hydroxide and 3.469 g of aluminium sulphate in 400 ml of water (or methanol) was heated under reflux for 1 h with vigorous magnetic stirring. The synthesis of the complexes gives lacquers containing K_2SO_4, which may be eliminated in the same way as for complex **5**. The lacquer obtained in these conditions presents three different hydration forms showing only one NMR signal for H_2O and Al—OH—Al in DMSO solution: $\delta OH = 3.34 \pm 0.02$ ppm (s, 26H, 14H or 4H according to the complex), $\delta H_3 = 6.55$ ppm (d, 8.0 Hz, 4H) and $\delta H_4 = 7.48$ ppm (d, 8.0 Hz, 4H), four equivalent pairs of AB systems, $\delta H_{6,7} = 7.75$ ppm (m, 8H), $\delta H_{5,8} = 8.12$ ppm (m, 8H).

Open structure binuclear complexes with $Ba(OH)_2 \cdot 8H_2O$ (complex 10). A solution of 5 g of alizarin, 8.20 g of barium hydroxide and 2.5134 g of aluminium chloride ($AlCl_3 \cdot 6H_2O$) in 400 ml of water (or methanol) was heated under reflux for 1 h with vigorous magnetic stirring. After filtration of the hot solution, the precipitate obtained was washed with hot water. This solid lacquer occurs in three different hydration forms showing only one NMR signal for H_2O and Al—OH—Al in DMSO solution: $\delta OH = 3.34 \pm 0.02$ ppm (s, 26H, 14H or 8H according to the complex), $\delta H_{3'} = 6.35$ ppm (d, *ca.* 7.7 Hz, 2H), $\delta H_3 = 6.63$ ppm (d, 8.1 Hz, 2H) and $\delta H_{4'} = 7.41$ ppm (d, *ca.* 7.8 Hz, 2H), $\delta H_4 = 7.49$ ppm (d, 8.0 Hz, 2H), two equivalent AB systems, $\delta H_{6,7} = 7.74$ ppm (m, 8H), $\delta H_{5,8} = 8.09$ ppm (m, 8H).

Open structure binuclear complexes with 1-hydroxy-2-methoxyanthraquinone (complex 11). A solution of 5 g of 1-hydroxy-2-methoxyanthraquinone, 1.182 g of sodium hydroxide and 3.28 g of aluminium sulphate in 400 ml of water (or methanol) was heated under reflux for 1 h with vigorous magnetic stirring. After standard treatment, the lacquer **11** obtained occurs in three different hydration forms showing only one NMR signal for H_2O and Al—OH—Al in DMSO solution: $\delta OH = 3.34 \pm 0.02$ ppm (s, 26H, 14H or 4H according to the complex), $\delta CH_3 = 3.74$ ppm (s, 12H), $\delta H_3 = 6.73$ ppm (d, 8.0 Hz, 4H) and $\delta H_4 = 7.11$ ppm (d, 8.0 Hz, 4H), $\delta H_{6,7} = 7.71$ ppm (m, 8H), $\delta H_5 = 8.04$ ppm (m, 4H) and $\delta H_8 = 8.19$ ppm (m, 4H).

Synthesis of 1-hydroxy-2-methoxyanthraquinone (3). A 1.5 g amount of alizarin and 0.25 g of sodium hydroxide were dissolved in 80 ml of dimethylformamide. An excess of CH_3I was added slowly with stirring at room temperature. The reaction was followed by thin-layer chromatography. The product was crystallized from CCl_4 (m.p. 228–230 °C). The NMR spectrum was obtained in $CDCl_3$ solution: $\delta OH = 12.98$ ppm (s, 1H), $\delta CH_3 = 3.95$ ppm (s, 3H), $\delta H_3 = 7.12$ ppm (d, 8.4 Hz, 1H) and $\delta H_4 = 7.82$ ppm (d, 8.4 Hz, 1H), $\delta H_{6,7} = 7.74$ ppm (m, 2H) and $\delta H_{5,8} = 8.25$ ppm (m, 2H).

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