

SPECTROSCOPIC PROPERTIES OF A NOVEL FLUORESCENT COMPLEX OF ALUMINIUM AND QUINIZARIN

NORMAN S. ALLEN, GERALD HAYES, PHILIP N. K. RILEY and
ANDREW M. RICHARDS

*Department of Chemistry, John Dalton Faculty of Technology, Manchester Polytechnic,
Chester Street, Manchester M1 5GD (U.K.)*

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Summary

The addition of aluminium compounds to 1,4-dihydroxyanthraquinone (quinizarin (QH₂)) in either aqueous or non-aqueous solutions results in the formation of a highly fluorescent pink-red complex with excitation maxima at 500, 530 and 573 nm and corresponding emission maxima at 585 and 619 nm. Analysis by absorption spectroscopy using mole ratio and continuous variation techniques indicates the formation of 1:1 and 2:1 Al:QH₂ complexes. Fluorescence quantum yields in excess of 0.8 have been measured in *n*-butanol. Observations on the stability and the spectroscopic properties of the 2:1 complex are presented, together with a plausible structure.

1. Introduction

It is a well known phenomenon that many types of organic ligands combine with metal ions to form metal chelates which are highly fluorescent. In most cases the fluorescence is the property of the organic ligand but is greatly intensified and often bathochromically shifted by the chelation to the metal ion. Aluminium is one of the most prolific of cations that form fluorescent metal chelates and these normally have either 1:1 or 1:2 aluminium:ligand stoichiometry. Numerous papers have appeared within the last 50 years documenting the formation of fluorescent metal chelates containing aluminium ions and various types of azo-dye molecules [1 - 8]. The formation of fluorescent metal chelates with anthraquinone derivatives is also well documented, particularly with the hydroxy derivatives. It is well known that thorium and beryllium give fluorescent complexes with 1,2,5,8-tetrahydroxyanthraquinone (quinalizarin) and 1,5- and 1,8-dihydroxyanthraquinones. However, such complexes only appear to be formed in concentrated acid or alkaline media [9]. It has been reported that quinalizarin produces a fluorescent complex with aluminium but that this is destroyed on addition of acid [1, 10].

In our research on the sensitivity and specificity of chelates for the fluorescence analysis of metal cations we have discovered that an interesting and novel phenomenon occurs when aluminium compounds are added to 1,4-dihydroxyanthraquinone (quinizarin (QH_2)). Addition of an aluminium compound to QH_2 in either aqueous or non-aqueous solution results in the formation of a pink-red complex with a fluorescence which increases in intensity with increasing molar ratio of aluminium to quinizarin and in some instances also develops with time. The related ligand 1-amino-4-hydroxy-anthraquinone exhibits similar behaviour but the fluorescence is less intense.

It is surprising that these observations have not been reported in the literature; this may be related to the conditions employed in analytical procedures and preparative methods for anthraquinone derivatives. A report [9] on the use of QH_2 in the fluorometric determination of beryllium in ores noted interference from aluminium, which provided an increased fluorescence and a salmon pink colour. Various derivatives of hydroxyanthraquinone other than QH_2 were tested for the fluorometric determination of

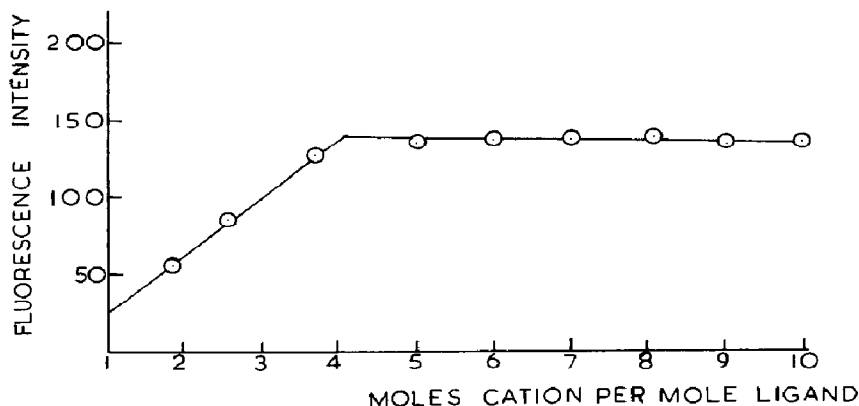


Fig. 1. Fluorescence at 573 nm vs. mole ratio of AlCl_3 to QH_2 in MeOH.

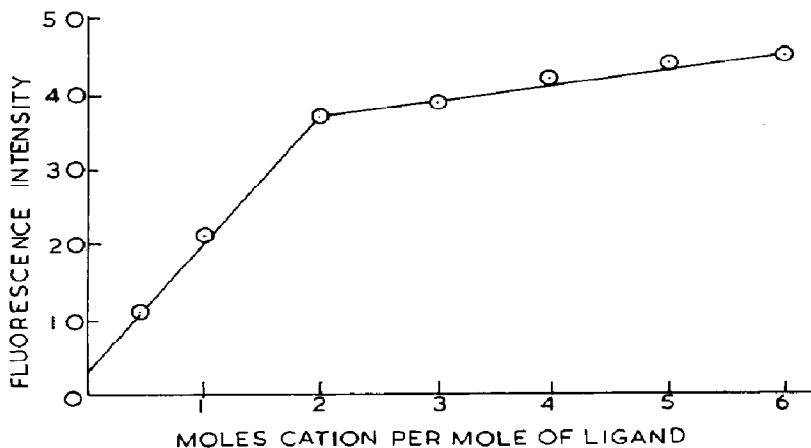


Fig. 2. Fluorescence at 573 nm vs. mole ratio of $\text{Al}(\text{acac})_3$ to QH_2 in MeOH.

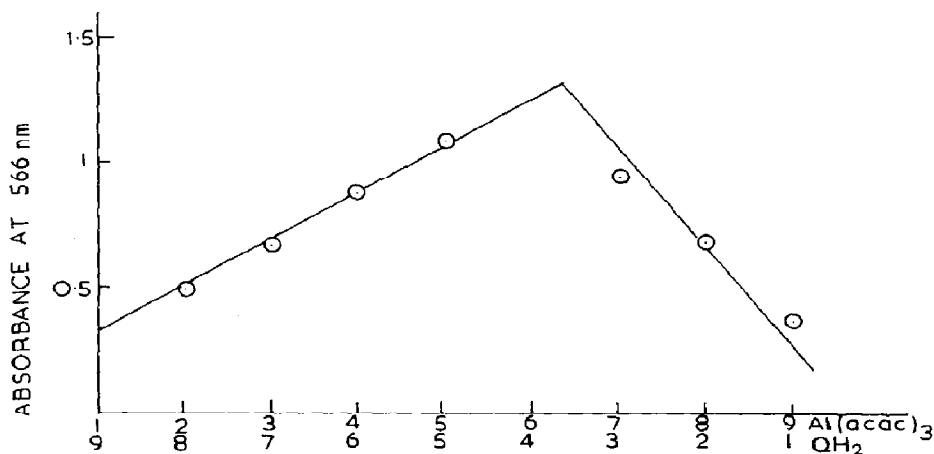


Fig. 3. Continuous variation: absorption at 566 nm of $\text{Al}(\text{acac})_3\text{-QH}_2$ solution in MeOH.

aluminium under alkaline conditions, and it was reported that addition of acid removes the fluorescence [11]. In this paper we report preliminary results on the formation of a novel fluorescent 2:1 complex between aluminium and QH_2 in several solvents. Mole ratio and continuous variation techniques indicate the formation of 1:1 and 2:1 complexes (Figs. 1 - 3). Although the exact nature of the complex has yet to be established, a plausible structure is presented.

2. Experimental details

2.1. Materials

AlCl_3 (anhydrous) and tris(pentan-2,4-dionato)aluminium(III) ($\text{Al}(\text{acac})_3$) were obtained from the Aldrich Chemical Co. Ltd. The latter was recrystallized from ethanol. $\text{Al}_2(\text{SO}_4)_3$ (the hexahydrate) was of AnalaR quality and was obtained from Fison Limited, U.K.

2.2. Solutions

A range of mixtures of the reactants, $\text{Al}(\text{acac})_3$ and QH_2 , with 2 cm³ increments up to a total volume of 20 cm³ was used for the continuous variation study, and mixtures containing 1 cm³ QH_2 solution and increasing volumes of the aluminium solutions made up to a total volume of 20 cm³ were used for the mole ratio study. All mixtures were employed directly for visible absorption spectroscopy and diluted ten times for measurement of fluorescence. Solvent effects were studied by preparing the solutions using several different solvents.

2.3. Spectroscopic measurements

Normal and derivative absorption spectra were obtained using a Perkin-Elmer model 554 spectrophotometer. Fluorescence excitation and emission spectra were obtained using a Perkin-Elmer LS-5 spectrofluorometer

coupled to a 3600 data station for spectral collection. Fluorescence quantum yields were obtained by the relative method using rhodamine B in ethanol as a standard [12, 13]. The quantum yield of the rhodamine B was assumed to be 0.70 and the excitation wavelength used was 530 nm. IR spectra were obtained using a Perkin-Elmer model 1420 ratio recording spectrometer.

3. Results and discussion

The absorption spectrum of QH_2 in ethanol is shown in Fig. 4 as a broad absorption band with shoulders on the long-wavelength side and a small peak at 490 nm. Addition of $AlCl_3$ shifts the absorption bathochromically and the spectrum shows three separate absorption peaks at 1:2 $Al:QH_2$. On further additions of $AlCl_3$ the spectrum changes again to two sharp absorption bands at 570 and 528 nm. The bands at 570 and 528 nm increase in intensity and broaden with increasing additions of $AlCl_3$ whereas the band at 494 nm does not change in intensity.

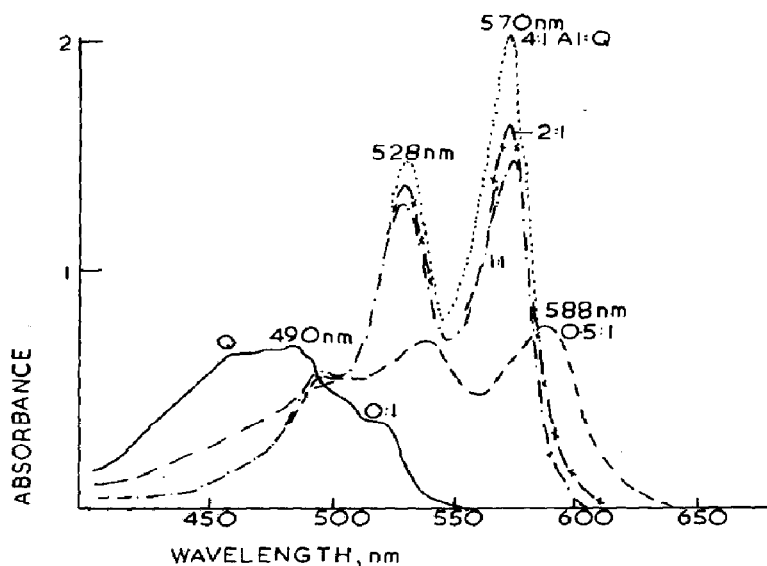


Fig. 4. Normal absorption spectra of ethanol solution of $AlCl_3$ and QH_2 at mole ratios of 0:1 (—), 0.5 (---), 1:1 (- · -), 2:1 (- x -) and 4:1 (.....). Total concentration, 2.25×10^{-4} M.

The second-order derivative spectra of QH_2 and $AlCl_3$ in *n*-butanol (Fig. 5) show the marked increase in intensity with increasing formal mole ratio.

Similar results have been obtained in aqueous solution with both $AlCl_3$ and $Al_2(SO_4)_3$. $Al(acac)_3$ was used to make up solutions containing aluminium in a range of organic solvents. Mixing with solutions of QH_2 produced similar sharp absorption bands at 573 and 530 nm and a weak

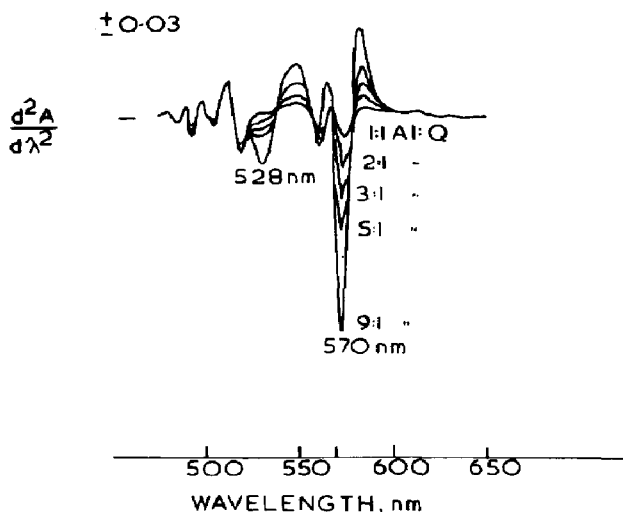


Fig. 5. Second-order derivative absorption spectra of solutions of AlCl_3 and QH_2 at various mole ratios in *n*-butanol.

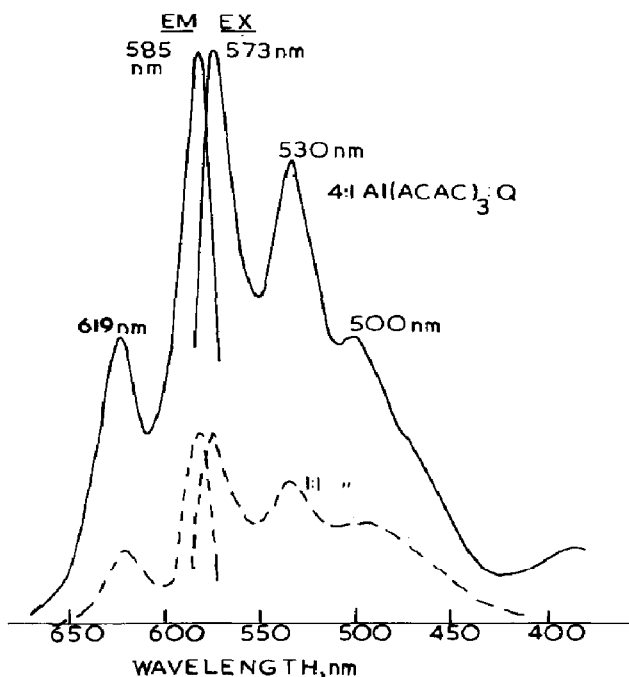


Fig. 6. Fluorescent excitation (EX) and emission (EM) spectra of $\text{Al}(\text{acac})_3$ and QH_2 at mole ratios of 4:1 (—) and 1:1 (---) in *n*-butanol (2.25×10^{-5} M).

shoulder at 500 nm. All the peaks showed an increase in intensity as the formal mole ratio ($\text{Al}:\text{QH}_2$) increased. Figure 6 for *n*-butanol solution is indicative of the results obtained in all the solvents. Unlike the observations with AlCl_3 there is little difference between the peak maxima for ratios of 1:1 and 4:1. The pink-red fluorescence exhibited by all the mixtures is

shown in Fig. 6 for *n*-butanol. The intensity also shows a dependence on the Al:QH₂ formal mole ratios, with emission maxima at 585 and 619 nm corresponding to complex formation at 2:1 ratios. The similarity between the absorption and the emission spectra obtained with different species containing aluminium and in different solvents points to the formation of a structurally similar product in each case. The small Stokes shift of about 12 nm between the wavelengths of excitation and emission maxima indicate the presence of a similar structure in both the ground state and the excited state [13].

The transfer of the complex between aqueous and non-aqueous solvents was investigated using *n*-pentanol. Al(acac)₃ and QH₂ in *n*-pentanol formed the complex. Solvent extraction with water produced no change in the organic layer. However, extraction with an aqueous solution of Al₂(SO₄)₃ resulted in the disappearance of the pink-red fluorescence, leaving a solution of QH₂ in the organic phase. Conversely, the pink-red fluorescence in aqueous solution produced using Al₂(SO₄)₃, and QH₂ disappeared on extraction with *n*-pentanol, resulting in a solution of QH₂ in the organic solvent.

Solid products have been obtained from organic solvents using both Al(acac)₃ and AlCl₃ and from an aqueous solution of Al₂(SO₄)₃. The solids are dark red to pale pink in colour. The product from AlCl₃ in alcohols turns from dark red to blue on standing; both solids redissolve in the organic solvent to re-form pink-red fluorescent solutions. However, when dissolved in water hydrolysis occurs with the separation of a hydroxide lake with the AlCl₃ complex, whereas the Al(acac)₃ product remains clear on dissolving in water. IR spectra were obtained using KBr discs of the solids. The red and blue solids containing AlCl₃ produced similar spectra differing only in the profile of a broad absorption band around 3500 cm⁻¹: the solids appear to differ in solvation only. The spectra also clearly show the presence of AlCl₄⁻ with a broad strong absorption band around 600 cm⁻¹ which is not present in the spectra of the other solids. The spectrum of the complex from Al₂(SO₄)₃ also shows evidence of both free and bidentate sulphate in the region around 1100 cm⁻¹. The products from Al(acac)₃ in alcohols from methanol to *n*-pentanol give identical spectra. In the region below 1700 cm⁻¹ the product spectra are similar to the superimposition of the spectra of QH₂ and Al(acac)₃ with a splitting at 1490 cm⁻¹ and 1300 cm⁻¹ in the broad strong bands between 1600 cm⁻¹ and 1300 cm⁻¹ in Al(acac)₃.

The IR spectra of QH₂ in non-polar solvents contain absorption bands which may be assigned to the carbonyl group (1710 cm⁻¹) and the phenol group (1355 cm⁻¹ and 1215 cm⁻¹) as well as to ring modes in the same region. The spectrum of solid QH₂ in a KBr disc resembles the spectra of the quinizarin complexes. The carbonyl stretch (1710 cm⁻¹) is absent in both but two strong absorptions occur around 1625 cm⁻¹ and 1580 cm⁻¹. The phenolic absorptions are also split into two strong bands (1360 cm⁻¹ and 1330 cm⁻¹ and 1255 cm⁻¹ and 1220 cm⁻¹) (Fig. 7).

These observations are interpreted as being evidence for the formation of cyclic intramolecular hydrogen bonds in solid QH₂ and similar ring systems with aluminium heterocations in the red fluorescent complexes.

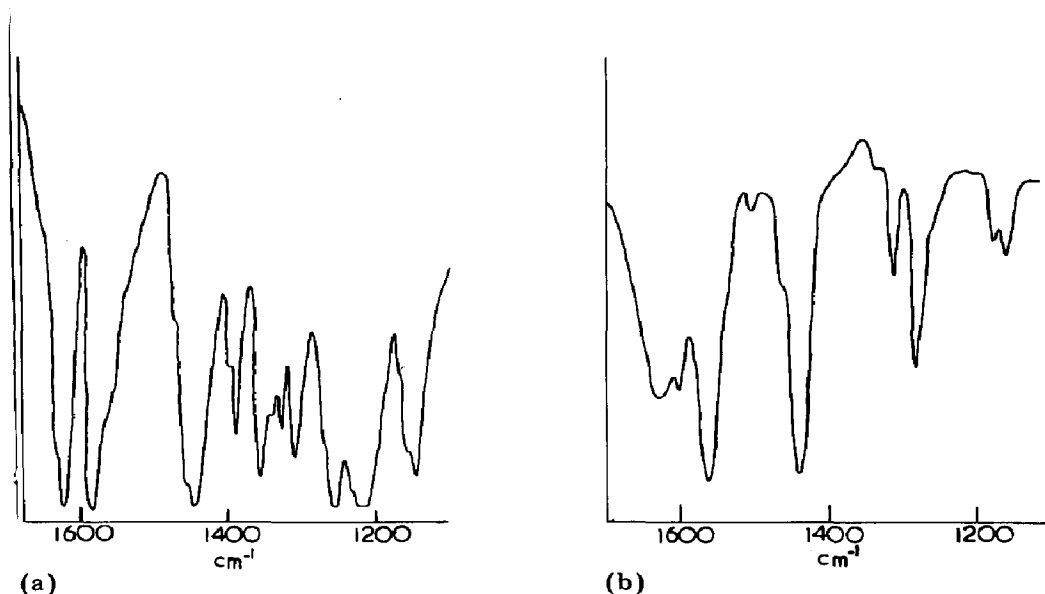


Fig. 7. IR absorption spectra in the region $1700 - 1100 \text{ cm}^{-1}$ for (a) QH_2 and (b) $\text{AlCl}_3\text{-QH}_2$ at a mole ratio of 4:1 in a KBr disc.

Quinalizarin and other anthraquinone derivatives have been used in the spectrophotometric determination of boron using sulphuric acid as a solvent [14]. The use of mixtures of boric acid and sulphuric acid in the preparation of anthraquinone derivatives is well established [15]. A solution of QH_2 ($1 \times 10^3 \text{ M}$) in concentrated sulphuric acid has an appearance similar to that of the pink-red complexes formed with aluminium compounds. Addition of boric acid results in a similar fluorescence. The absorption spectra show only small differences in peak maxima and the emission peaks and profiles for QH_2 with mixtures of boric acid and sulphuric acid and with AlCl_3 in methanol are also similar.

4. Conclusions

The QH_2 molecule contains two phenolic groups which with the two keto groups appear to be involved in the formation of chelates with aluminium species in the solutions used in this investigation. Similar dye molecules, 1-amino-4-hydroxyanthraquinone and 1,4-diaminoanthraquinone, were examined under the same conditions. The former showed similar behaviour but the fluorescence intensity was much less, whereas the latter did not exhibit fluorescence.

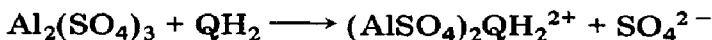
AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$ are well known for producing heterocations, e.g. AlCl_2^+ and AlSO_4^+ , in solution. The behaviour of solutions of the chloride in acetonitrile [16] has been interpreted in terms of the species $[\text{AlCl}_2(\text{CH}_3\text{CN})_n]^+\text{AlCl}_4^-$. It is suggested that the active fluorescent species may be derived in a similar way by the chelation of QH_2 .

The 1:1 cation $\text{AlCl}_2\text{QH}_2^+$ may be formed initially but it is proposed that the species producing the observed phenomenon is formed by



The formal 4:1 ratio of AlCl_3 to QH_2 in this equation may be correlated directly with the mixing ratios of the solutions (Fig. 1).

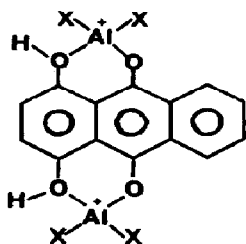
The structure proposed could also be formulated with AlSO_4^+ and $\text{Al}(\text{acac})_2^+$, *i.e.* the common fluorescent structure is QH_2 doubly chelated to two separate Lewis acids AlX_n^+ in the ratio 2:1 (Fig. 3)



or



Adsorption onto activated alumina from solution or by shaking a solid mixture produces the same pink-red colour which may be related to chelation on adjacent Lewis acid sites at the surface.



A formulation using the undissociated QH_2 is proposed because the anion Q^{2-} formed on addition of alkali produces an intensely blue solution. The pink-red product can be obtained in buffer solutions of pH less than 4 in which proton dissociation is unlikely. Further, if dissociation of the phenolic groups occurs the neutral compounds formed should be solvent extractable. The formation of such complex cations may be favoured in the organic solvents used but is less likely in aqueous solution. In this case cationic hydrolytic species containing aluminium may combine with QH_2 .

The cationic hydrolytic species formed in aqueous solution depend on both pH and pAl. The relative concentrations of the different species and the pK values have been calculated and compared with experimental data [17, 18]. At this stage of the investigation it only requires the presence of the species $\text{Al}(\text{OH})_2^+$ to formulate a combination similar to that proposed above for non-aqueous solvents: $[\{\text{Al}(\text{OH})_2\}_2\text{QH}_2]^{2+}$. The isolation of such species may be accomplished by the addition of an appropriate counter-anion.

The association between the heterocations and QH_2 can be broken by extraction of the QH_2 from aqueous solutions and by extraction of the aluminium from non-aqueous solutions.

It is proposed that QH_2 in non-polar solvents behaves as a molecule with no intramolecular hydrogen bonding. Dissolution in polar solvents will result in competition for hydrogen bonding. Intermolecular hydrogen

bonding will stabilize the ground state, resulting in a hypsochromic shift in the absorption maxima, as is observed between toluene and methanol solutions (20 - 25 nm). The bathochromic shift in concentrated sulphuric acid is 30 - 33 nm (*cf.* toluene solution) and may be related to protonation of the keto group and the formation of a hydrogen-bonded ring.

Replacement of the proton by other solvated heterocations suggests that a range of similar complexes may exist. We are investigating potential heterocations derived from EX_3 , EX_5 and E_2O_3 compounds as well as the applications of the Al-QH₂ complexes.

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