Chelates of Aluminium(III) with 2-Methylquinolin-8-ol

By PAUL R. SCHERER and QUINTUS FERNANDO*
(*Department of Chemistry, University of Arizona, Tucson, Arizona,* 85721)

THE failure of aluminium(III) to form an insoluble precipitate or an extractable complex with 2-methylquinolin-8-ol has been exploited during the past 20 years for the separation and determination of aluminium in the presence of a variety of metal ions. Merritt and Walker[1] first reported in 1944 that, although aluminium(III) reacted readily with 8-quinolinol to form a 1 : 3 complex, no reaction occurred with 2-methylquinolin-8-ol. In 1949, Irving and his co-workers[2] attributed this non-reactivity to steric hindrance caused by the 2-methyl group in the packing of 2-methylquinolin-8-ol molecules around the small aluminium ion. Failure to form even a 1 : 1 aluminium complex in aqueous solution also arises from a steric effect between the methyl group of the 2-methylquinolin-8-ol and the sheath of water molecules around the aluminium ion.[3] It is difficult however, on the basis of steric effects alone, to explain the ready formation of the 1 : 3 metal complexes of gallium(III) and indium(III) on the one hand, and on the other hand the non-reactivity of aluminium(III) with 2-methylquinolin-8-ol.[3] Irving and Pettit also summarized other anomalies that have been observed in the reactions of 8-quinolinol-type ligands with metal ions.[3]

Despite the widespread acceptance of the theory that steric effects prevent the reaction of aluminium(III) with 2-methylquinolin-8-ol, there have been a few reports which indicate that complex formation does indeed occur. For example, the fluorescence observed in a melt containing aluminium(III) and 2-methylquinolin-8-ol,[4] or in the chromatography of aluminium(III) on paper impregnated with 2-methylquinolin-8-ol,[5] indicate that there is an interaction between the aluminum ion and 2-methylquinolin-8-ol, but it cannot be definitely attributed to complex formation. However, fluorescence measurements in an absolute ethanol medium containing aluminium(III) and 2-methylquinolin-8-ol provided more conclusive evidence for the presence of a 1 : 1 metal complex.[6] The fusion products of aluminium chloride and 2-methylquinolin-8-ol also indicate that a compound with an aluminium–oxygen bond is present.[7] Up to date however, no complexes of aluminium(III) have been isolated and characterized. We report here the preparation and characterization of two such complexes.

Aluminium chloride (0·1 mole) was added to a solution of 2-methylquinolin-8-ol (0·3 mole) and diethylamine (0·3 mole) in chloroform. The reaction was allowed to proceed in an atmosphere of dry nitrogen. Two crystalline compounds were isolated from the yellow solid that separated from the reaction mixture.

Compound (I). $Al(C_{10}H_8ON)_2,OH,CHCl_3$ (yellow orthorhombic crystals). Found: C,52·7; H, 3·8; N, 5·8. Calc.: C, 52·52; H, 3·78; N, 5·84%.

This compound showed a strong yellow-green fluorescence in ultraviolet light and formed orthorhombic crystals in the space group *Pbcn*. The cell dimensions as determined from Weissenberg photographs with Cu-K_α radiation are as follows: a = 13·08, b = 10·00, and c = 16·54 Å. The density determined by flotation is 1·45 and the molecular weight calculated for four molecules in the unit cell is 472 (theoretical value 480). A bromometric titration was carried out in an aqueous HCl medium containing an excess of NaBr with electrogenerated bromine and an amperometric indicator system.[8] The results confirmed the presence of two moles of 2-methylquinolin-8-ol per mole of the metal complex. The compound was ignited at 600° in a muffle furnace and the residue dissolved in hot concentrated HNO_3; the aluminum in the solution was determined[9] by back titration of the excess of EDTA with Hg^{2+}, and the presence of one mole of aluminum per mole of the metal complex was confirmed. The orthorhombic crystals were introduced into a Hitachi–Perkin Elmer RMU 6E mass spectrograph and warmed to 92°. The characteristic fragmentation pattern of $CHCl_3$ was observed. Furthermore, when the crystals were heated in an oven at 110°, the compound reached a constant weight after 7 hr. The 25% loss in weight confirmed the presence of a mole of chloroform per mole of metal complex.

Compound (II). $[Al(C_{10}H_8ON)_2,OH]_2$ (pale yellow monoclinic crystals). Found: C, 66·7; H, 4·7; N, 7·9. Calc.: C, 66·67; H, 4·75; N, 7·77%.

This compound crystallized in space group *Cc* or *C2/c*. The cell dimensions as determined from Weissenberg photographs with Cu-K_α radiation are: a = 30·75, b = 12·45, c = 16·07 Å, and β = 104·8°. An accurate value of the density could not be determined by flotation owing to solubility of the very small needle-shaped crystals in the solvents used. A bromometric titration confirmed the percentage of 2-methylquinolin-8-ol in the metal complex.

The ^1H n.m.r. spectrum on a Varian A.60 spectrometer of 2-methylquinolin-8-ol and compound (II) were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. The spectra of both compounds showed the presence of the protons in the methyl group at 2·6 p.p.m. The presence of the phenolic proton at 8·35 p.p.m. could not be detected in the spectrum of the metal complex, but an additional peak at 2·45 p.p.m., with an area 1/6th that of the peak arising from the methyl group protons, was present and could be attributed to the protons in the hydroxy-groups co-ordinated to the aluminium ion. A ^1H n.m.r. spectrum of the orthorhombic crystals, compound (I), could not be obtained owing to its poor solubility in $CDCl_3$.

Chelate formation between 8-quinolinol type ligands and metal ions gives rise to certain characteristic features in the infrared spectra of the resulting metal complexes. A strong band in the infrared spectra of the metal complexes in KBr, arising from the aluminium–oxygen–carbon vibrational modes, at 1110 cm.$^{-1}$ is present in the spectra of the metal complexes (I) and (II) but absent in the free ligand spectrum. A very strong band at 1186 cm.$^{-1}$, attributable to the stretching frequency of the phenolic hydroxy-group in the ligand, is absent in the spectra of both metal complexes. No absorption bands between 3200 and 2500 cm.$^{-1}$, arising from N–H stretching modes, are present in the spectra of both complexes.

All the above evidence shows that the metal complexes that have been isolated have a definite stoicheiometry and are probably 1 : 2 chelates of aluminium(III) and 2-methylquinolin-8-ol. If the aluminium ion is hexaco-ordinated in these two complexes, the monoclinic compound is a hydroxy-bridged dimer and the orthorhombic compound is the monomer with a molecule of chloroform occupying the vacant sixth position in the co-ordination sphere of the aluminium ion. Conclusive evidence for these postulated structures must await complete single crystal structure determinations of these compounds. In an attempt to carry out a structure determination of the orthorhombic compound we have encountered an unusual difficulty. On exposure to Cu-K_α radiation, the space group changes and one of the axial lengths is doubled. It is possible that this change in the space group arises from a dimerization reaction in the crystal. Unfortunately the structures in both space groups show a certain amount of disorder. Attempts to obtain single crystals of chelates of aluminum(III) with substituted 2-methylquinolin-8-ols that are suitable for an *X*-ray structure determination are in progress.

This work was supported by the U.S. Atomic Energy Commission.

(*Received, September 4th,* 1967; *Com.* 944.)

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