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Preliminary communication

THE REACTION OF ALUMINIUM TRICHLORIDE WITH 9,10-PHENANTHROQUINONE

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Summary

A persistent radical formed by the title reaction has been characterised by ESR.

Although a recent assignment [1] of an ESR spectrum to an aluminium-containing free radical has been queried [2], persistent radicals containing aluminium are not unknown. It was reported several years ago that complexes exhibiting well resolved coupling to ^{27}Al (I = 5/2) are formed in the reactions of aluminium halides [3] and alkyls [4] with 3,5-di-t-butyl- or 3,6-di-t-butyl-1,2-benzoquinone. Similar radicals have also been reported containing Ga and In [3,4,5]. Kabachnik and his coworkers [6] have observed temperature dependent effects attributed to "floating valence" in the ESR spectrum of an aluminium catecholate complex.

The current interest in aluminium containing radicals prompts us to report some observations [7] on a persistent radical formed in the reaction of 9,10-phenanthroquinone (PQ) with $AlCl_3$. Admixture of dilute solutions of the two reactants in diglyme or THF leads to the rapid development of a green colouration* and a strong ESR signal.

The resolution of the spectrum varied with time, temperature and solvent but under optimum conditions could be readily interpreted in terms of coupling to two sets of four equivalent protons (0.2 mT and 0.045 mT) and to a single ^{27}Al nucleus (0.205 mT). Spectra could be observed up to 140°C in diglyme but the radical was less thermally stable in THF. The ESR signal persisted at room temperature for several days during which time the solution became increasingly gelatinous. We assign the spectrum to the complex I existing either

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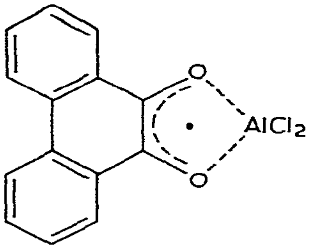
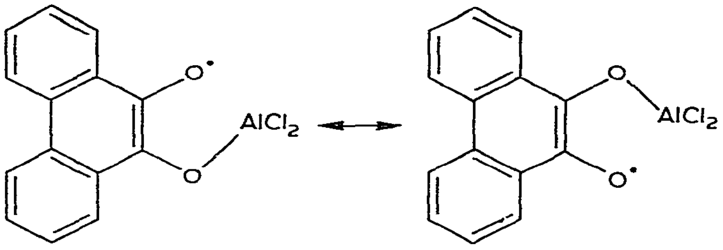
*First reported by Meyer [11].



(Ia)



(Ib)

as a four-coordinate species Ia or as a rapid equilibrium between equivalent tautomers Ib. In the case of analogous tin complexes it has been established that either possibility can be realised, depending on the nature of the substituents on the metal [8,9]. The two situations can be distinguished if it is possible to slow down the rate of exchange in Ib so that line broadening is apparent in the ESR spectrum. This proved possible in the study of the aluminium complex reported by Kabachnik et al. [6] but we have been unable to detect any alternating linewidth effect in the ESR spectrum of I. A possible clue, however, is provided by the absence of any resolvable chlorine hyperfine coupling in the ESR spectrum. In the studies of the tin derivatives of semiquinones [8] and semidiones [9] referred to above, ^{35}Cl splitting was detected in species containing five coordinate tin (cf. Ia) but not in complexes exhibiting tautomerism (cf. Ib). We therefore conclude that, if the analogy is valid, the complex I exists as a pair of tautomers Ib with a low barrier to interconversion. Complexation of a solvent molecule to the metal, thereby increasing the coordination number of the aluminium from three to four, may well be important in stabilising the adopted structure. Interestingly, complexes formed from $AsCl_3$ and $SbCl_3$ exhibit coupling of ca. 0.1 mT to two equivalent chlorine atoms [10].

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