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Spectroscopic and crystallographic studies of adducts of aluminium trichloride with cyclic ketones, *para*-quinones and *ortho*-quinones

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Adducts of aluminium(III) chloride with 9-fluorenone, xanthenone and dibenzosuberenone have been characterised spectroscopically and by single crystal X-ray crystallography. These coloured pseudo-tetrahedral species, which are diamagnetic in both solid and solution states, serve as models for 1 : 1 adducts of $AlCl_3$ with substituted *p*-quinones. These latter compounds undergo intramolecular one-electron transfer in non-aqueous solution, giving rise to paramagnetic species which have been characterised by electron spin resonance spectroscopy. The 1 : 1 adducts of $AlCl_3$ with *o*-quinones show similar behaviour, although the solution chemistry reflects the differences between mono- and bi-dentate ligands.

The formation of adducts of aluminium trihalides with both neutral and anionic donors has been an intensively studied area of Main Group inorganic chemistry, both because of the importance of such compounds in understanding the fundamentals of donor–acceptor interactions, and their significance in the chemistry of Friedel–Crafts catalysis. Four- five-, or six-co-ordinate complexes may be obtained, depending in part on the nature of the donor ligand and on the trihalide in question.[1] We now report preparative and spectroscopic studies of the adducts which are formed with *para*- and *ortho*-quinones, carried out as part of a continuing programme of work on the addition of these oxygen donors to metal halide acceptors, and of the electron transfer processes which may follow co-ordination. The behaviour of some analogous derivatives with cyclic ketones is relevant to this investigation, in which both X-ray crystallography and electron spin resonance (ESR) spectroscopy have been important experimental tools.

The interpretation of the results is derived from related work on the interaction of *ortho*- and *para*-quinones with indium(III) halides.[2] In all of these systems intramolecular one-electron transfer is a key feature of the reaction mechanism.

Experimental

All reagents were Reagent Grade or better, and were used as supplied. Solvents were purified by standard procedures. Reactions were carried out in an atmosphere of dry nitrogen, using the conventional techniques for handling potentially air-sensitive materials.

Microanalysis was carried out by Canadian Microanalytical Services Ltd. Infrared spectra were recorded, as KBr discs, using a Nicolet 5DX instrument, and electron spin resonance spectra on a Bruker ESP-300E spectrometer, using the experimental and calibration techniques described elsewhere.[3]

Preparative techniques

The preparation of all the adducts described involved small variants of a simple procedure in which millimolar quantities of the reactants were mixed together in a suitable organic solvent (toluene, chloroform, dichloromethane, carbon tetrachloride) at room temperature. In each case, an immediate colour change was observed, and a sample of the solution was removed for ESR spectroscopy. Further samples were taken later. In some cases a solid precipitated when solutions of the reactants were mixed, while in others products were obtained either by slow removal of solvent or by cooling (see Table 1). In most cases it proved extremely difficult to redissolve the products in the reaction solvent. Analytical results and other data are given in Table 1.

Crystallographic studies

Samples of the adducts **1**, **2** and **3** were dissolved in dimethylformamide and allowed to recrystallise by slow evaporation of the solvent in air. For the fluorenone adduct **1** the instrument used was a Siemens SMART 3-circle diffractometer equipped with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71069$ Å) and a CCD area detector, and controlled by a Pentium-based PC running the SMART software package. Cell parameters were refined using the centroid values of 300 reflections with 2θ angles up to 56.62°. Raw frame data were integrated using the SAINT program. The structure was solved by direct methods. An empirical absorption correction was applied to the data using the program SADABS. The programs used are listed in refs. 4–7.

The crystallographic techniques used for the adducts **2** and **3** with 9-xanthenone and dibenzosuberenone involved suitable crystals mounted on a glass fibre in a Rigaku AFC6S diffractometer, equipped with Mo-Kα radiation and a rotating anode. Cell constants, and an orientation matrix, were obtained using 25 strong reflections in the range $12.66 < 2\theta < 15.52°$. Packing considerations, a statistical analysis of intensity distribution, and successful solution and refinement of the structure yielded the space group. Decay corrections were needed in each case; absorption corrections were applied, and the data were also corrected for Lorentz-polarisation effects. The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically; hydrogen atoms on carbon were included in ideal positions. The programs and other data used are listed in refs. 8–13.

Table 2 summarises the details of the crystallographic analysis, and important interatomic distances and angles are given in Table 3. The structures, and the numbering schemes are shown in Figs. 1–3.

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Table 1 Preparative and analytical details for 1 : 1 adducts of $AlCl_3$

Sample	Donor	Reaction solvent	Colour	Analysis[a]	
				C	H
1	9-Fluorenone	Toluene	Red	49.2 (49.8)	2.15 (2.55)
2	9-Xanthenone	$CHCl_3$	Pale pink	47.6 (47.3)	2.55 (2.45)
3	Dibenzosuberenone[b]	Toluene	Dark yellow	53.3 (53.0)	3.00 (2.95)
4	*p*-Benzoquinone[c]	Toluene	Black	29.4 (29.8)	1.90 (1.65)
5	Tetrachloro-*p*-benzoquinone[c]	Toluene	Yellow	18.4 (19.0)	0.10 (0)
6	Tetrabromo-*p*-benzoquinone	Toluene	Yellow	13.6 (12.9)	0.05 (0)
7	2,6-Di-*tert*-butyl-*p*-benzoquinone	$CHCl_3$	Black	47.2 (47.5)	5.80 (5.65)
8	1,4-Naphthoquinone[c]	$CHCl_3$	Black	41.3 (40.9)	2.30 (2.75)
9	3,5-Di-*tert*-butyl-*o*-benzoquinone	Toluene	Deep brown	47.6 (47.5)	5.80 (5.65)
10	1,2-Naphthoquinone	$CHCl_3$	Blue	40.5 (40.9)	2.15 (2.75)
11	9,10-Phenanthrenequinone	$CHCl_3$	Dark green	61.0 (58.3)	3.15 (3.45)

[a] %, found (calc.). [b] 5*H*-Dibenzo[*a*,*d*]cyclohepten-5-one. [c] Product precipitated immediately.

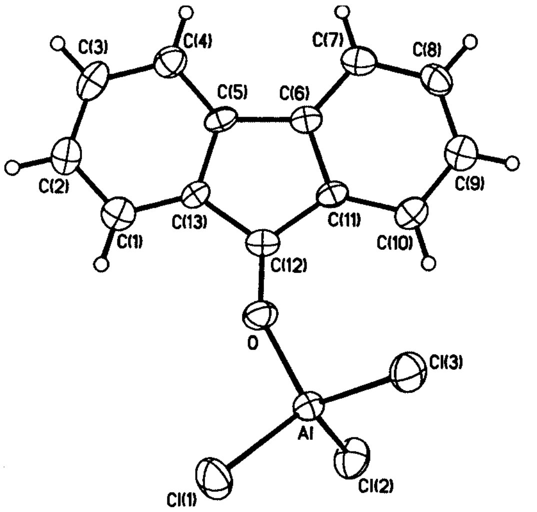

Fig. 1 Structure of the fluorenone adduct of $AlCl_3$, showing the numbering system; ORTEP diagram, with atoms shown as 30% probability ellipsoids.

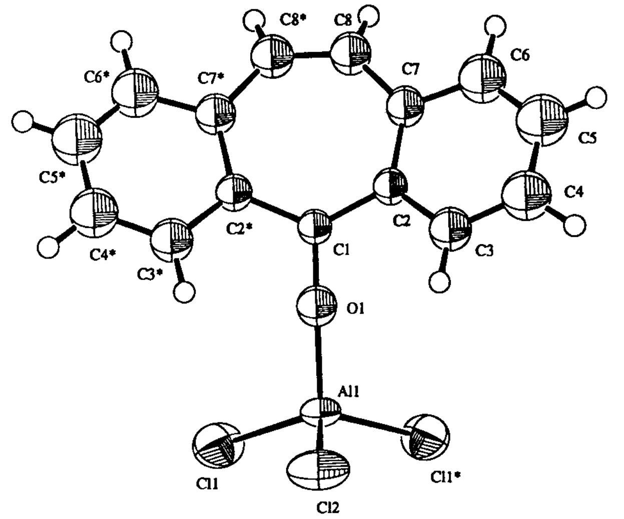

Fig. 3 Structure of the suberenone adduct of $AlCl_3$. Details as in Fig. 1.

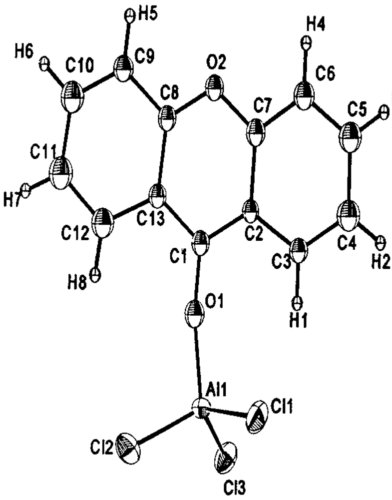

Fig. 2 Structure of the xanthenone adduct of $AlCl_3$. Details as in Fig. 1.

Results and discussion

Adducts with cyclic ketones

The existence of adducts of the aluminium halides with ketones has been well documented, and the justification for including them in the present study is that they represent a model for the oxygen donor–acceptor interaction, which is a significant aspect of the chemistry of the corresponding *para*- and *ortho*-quinone compounds. Both spectroscopic and crystallographic results bear on this aspect of the work.

The structure of each of the aluminium trichloride adducts shows the same essential features, namely C_{3v} symmetry at the aluminium centre, an Al–Cl bond distance in the range 2.066(10)–2.117(2) Å, and Al–O bond distances of 1.76(1)–1.79(1) Å. The C=O bond of each ketone shows significant lengthening in the adduct, compared with the parent molecule. For 9-fluorenone,[14] *r*(C=O) is reported to be 1.220(4) Å, and the value in the 1 : 1 adduct is 1.266(5) Å, while in the case of dibenzosuberenone the corresponding distances are 1.24(1) and 1.31(1) Å.† There does not appear to have been a determination of the structure of xanthenone, but for 1,3,4,6,7,8-hexachloro-9-xanthenone[15] *r*(C=O) is 1.211(13) Å, compared to 1.29(1) in the adduct. There is a lengthening of the order of 0.05 Å in these three cases, in keeping with the expected donation of electron density from the ketonic oxygen to the metal centre, and it seems reasonable to assume that a similar process occurs in the corresponding quinone adducts. It is important to note the significance of the acceptor molecule in such systems, since in the case of adducts of fluorenone and xanthenone with indium(III) iodide there is no significant change in *r*(C=O) on complexation.[16]

Comparisons between the structures of the cyclic ketones and those of the 1 : 1 adducts with aluminium trichloride show

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† A preliminary crystallographic study of dibenzosuberenone was performed using the same methods as for the adduct: monoclinic, space group *Cc*, $a = 21.607(7)$, $b = 3.944(3)$, $c = 14.469(4)$ Å, $\beta = 122.94(2)°$, $Z = 4$, $R' = 0.041$.

Table 2 Summary of crystal data, intensity collection and structure refinement for adducts **1**–**3**

	1	**2**	**3**
Formula	$C_{13}H_8AlCl_3O$	$C_{13}H_8AlCl_3O_2$	$C_{15}H_{10}AlCl_3O$
M	313.55	329.55	339.58
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	*Pbca* (no. 61)	$P2_1/n$ (no. 11)
a/Å	9.145(5)	19.926(2)	6.205(2)
b/Å	17.228(6)	17.280(2)	15.889(2)
c/Å	17.385(7)	9.544(1)	7.597(2)
β/°	—	—	91.59(3)
V/Å^3	2739(2)	2791.5(6)	748.7(4)
T/K	298	296	296
Z	8	8	2
μ/cm^{-1}	7.16	7.12	6.62
Total reflections measured	3809	2817	1503
Unique data used	1676	726	587
R′	0.0488	0.043	0.64

Table 3 Important bond lengths [Å] and angles [°] for the adducts $AlCl_3 \cdot L$

L = 9-Fluorenone			
Al–O	1.787(3)	O–Al–Cl(2)	107.27(14)
Al–Cl(2)	2.097(2)	O–Al–Cl(1)	105.23(14)
Al–Cl(1)	2.109(2)	Cl(2)–Al–Cl(1)	113.18(9)
Al–Cl(3)	2.117(2)	O–Al–Cl(3)	107.03(13)
O–C(12)	1.266(5)	Cl(2)–Al–Cl(3)	113.55(9)
		Cl(1)–Al–Cl(3)	110.00(9)
		C(12)–O–Al	150.2(3)
L = Xanthenone			
Cl(1)–Al(1)	2.118(4)	Cl(1)–Al(1)–Cl(2)	109.8(2)
Cl(2)–Al(1)	2.098(4)	Cl(1)–Al(1)–Cl(3)	112.1(2)
Cl(3)–Al(1)	2.116(4)	Cl(1)–Al(1)–O(1)	107.9(3)
Al(1)–O(1)	1.764(6)	Cl(2)–Al(1)–Cl(3)	113.3(2)
O(1)–C(1)	1.29(1)	Cl(2)–Al(1)–O(1)	107.7(3)
O(2)–C(7)	1.36(1)	Cl(3)–Al(1)–O(1)	105.7(3)
O(2)–C(8)	1.35(1)	Al(1)–O(1)–C(1)	160.0(7)
		C(7)–O(2)–C(8)	119.8(8)
		O(1)–C(1)–C(2)	119.9(9)
		O(1)–C(1)–C(13)	120.3(9)
L = Dibenzosuberenone			
Cl(1)–Al(1)	2.111(3)	Cl(1)–Al(1)–Cl(1*)	111.2(2)
Cl(2)–Al(1)	2.102(5)	Cl(1)–Al(1)–O(1)	109.3(2)
Al(1)–O(1)	1.762(9)	Cl(1)–Al(1)–Cl(2)	111.1(1)
O(1)–C(1)	1.31(1)	Cl(2)–Al(1)–O(1)	104.7(3)
		Al(1)–O(1)–C(1)	158.8(8)
		O(1)–C(1)–C(2)	114.6(5)

that there is very little change in the bond distances and angles within the cyclic framework, even in the region closest to the C=O bond. One constant structural feature of the adducts is the non-linear C–O–Al bonding; the bond angles in **1**, **2** and **3** are 150.2(3), 160.0(7) and 158.8(8)° respectively. It is assumed below that a similar non-linearity is present in the *p*-quinone adducts of $AlCl_3$.

The infrared spectra of these adducts show small changes in the ν(C=O) region, where the frequencies are 1714 (1710) for **1**, 1657 (1687) for **2** and 1595 (1647) cm^{-1} for **3**; the values in parentheses are for ν(C=O) of the free ketone. The changes (4, 30 and 52 cm^{-1} respectively) are in the same order as those in the C=O bond distances on complexation, and confirm the weakening of the C=O bond. We also examined the ESR properties of these adducts, given the behaviour of the quinone derivatives (see below). The xanthenone compound is ESR silent in both the solid and solution phases. The derivatives of fluorenone and dibenzosuberenone showed very weak activity in both phases in the free radical region of the spectrum, but no detailed information could be derived from these resonances, which we ascribe to minor impurities and/or decomposition products.

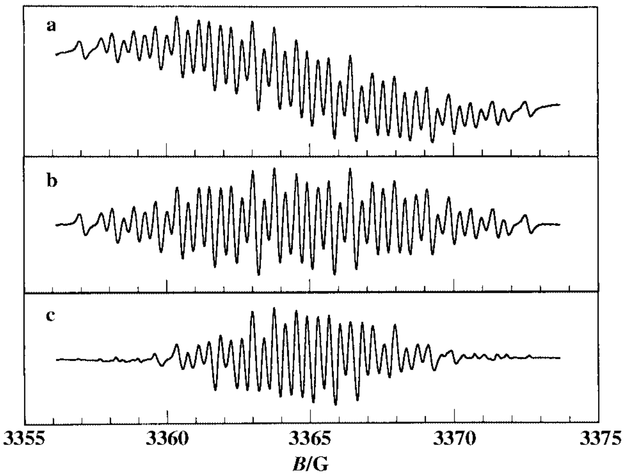


Fig. 4 (a) Room temperature ESR spectrum of a solution of $(p\text{-}C_6H_4O_2)AlCl_3$ in toluene. (b) Central portion of the same spectrum, after subtraction of broad line. (c) Spectrum (b) after subtraction of a simulated spectrum fitted to the outer lines of (b); parameters used are $g = 2.0039$, $A_{Al} = 0.77$ G, $A_H = 4.71$ G (2H), 1.12 G (2H).

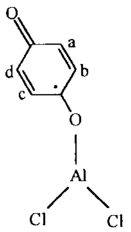
The general conclusion from these structural and spectroscopic results is that adduct formation with $AlCl_3$ produces the expected changes in the C=O bond of the cyclic ketones, and that these changes are compatible with donation to the metal centre, as are the colours which develop on complexation (see Table 1). There is no evidence for the one-electron transfer from donor to acceptor in these diamagnetic adducts. The results are in general agreement with the relevant features of studies of adducts of carbonyl compounds and $MeAl(BHT)_2$ and $R_2Al(BHT)OEt_2$ (R = Me or Et; BHT^- = 2,6-di-*tert*-butyl-4-methylphenolate).[17,18]

Adducts with *para*-quinones

The analytical results in Table 1 establish that $AlCl_3$ forms 1 : 1 adducts with five *p*-quinones with different substituents, and hence different redox properties. Unfortunately we were not able to obtain any of these complexes in sufficiently good crystalline form for characterisation by X-ray methods, so that the discussion rests upon the spectroscopic evidence alone.

There are small non-systematic changes in the ν(C=O) region of the infrared spectrum, in the order of 5–10 cm^{-1}, on complexation. These are similar to, but smaller than, those noted for the cyclic ketone adducts and although they do not lead to any detailed structural conclusions they do establish that in the solid *p*-quinone adducts the electron donation process is analogous to that in the ketone complexes. More importantly, no vibrations were detected in the C–O single bond region, so that complexation does not drastically affect the properties of the C=O bond in the solid state. These results are analogous to those reported earlier for *p*-quinone adducts of indium(III) iodide.[2]

The solid adducts show only very weak ESR activity, which is again attributed to the presence of impurities and/or decomposition products, but the spectra of solutions of these compounds show significant resonances in the free radical region. The interpretation of the results is hampered by the low solubility of these adducts, and hence weak spectra, in suitable solvents. Fig. 4(a) is the spectrum of a dilute solution of $(p\text{-}C_6H_4O_2)AlCl_3$ in toluene at room temperature. This is clearly a solution phase spectrum superimposed on a broad line, and this latter is presumed to be due to colloidal material, or clusters of solute species. Subtraction of this broad feature produces the sharp multi-line spectrum shown in Fig. 4(b), and this itself was found to be composed of two independent solution spectra. The outer portion of Fig. 4(b) is well simulated with the parameters $g = 2.0039$, $A_{Al} = 0.77$ G, $A_{H1} = 4.71$ G (2H) and $A_{H2} = 1.12g$ (2H), assigned to the structure shown.

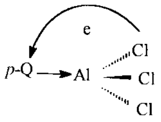


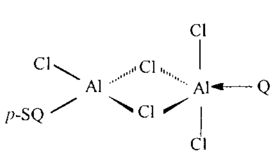
The two different pairs of hydrogen hyperfine constants are due to the non-linear C–O–Al bonding, identified earlier in the adducts of $AlCl_3$ with cyclic ketones, together with free rotation in the solution phase of the *p*-semiquinonate ligand around the Al–O bond. Further subtraction of this simulated spectrum from the experimental leaves Fig. 4(c), which can be imperfectly simulated with $A_{Al} \approx 0.8$ G, and A_H values lower than those quoted above. We return to this point below. A similar situation applies for the ESR spectrum of a solution of (p-$C_6H_2Bu^t_2O_2$)$AlCl_3$ in xylene. In this case the simulated parameters for the outer region of the spectrum are $g = 2.0040$, $A_{Al} = 0.45$ G, $A_H = 7.79$ G (2H), and again the remaining central portion of the spectrum is of a species with similar hyperfine constants.

We suggest that dissolution of these compounds is followed by reaction (1) which is the result of an intramolecular electron

$$(p\text{-Q})AlCl_3 \longrightarrow (p\text{-SQ}^{\bullet})AlCl_2 + Cl^{\bullet} \qquad (1)$$

transfer within the *p*-quinone adduct. A more detailed discussion of such processes has been given elsewhere, with particular reference to the effect of phase.[2] The halogen atom presumably reacts with the solvent, while the (p-SQ$^{\bullet}$)$AlCl_2$ species is that characterised in the ESR parameters quoted above for p-SQ$^{\bullet}$ = $C_6H_4O_2$ or $C_6H_2Bu^t_2O_2$. This semiquinone compound is clearly present in a non-aqueous solution of the 1 : 1 adduct, and it is probable that the formation of higher-order complexes such as that shown below will also occur, since a three-coordinate aluminium(III) centre is a strong electron-pair acceptor. A molecule of this type should give rise to hyperfine constants similar to those of (p-SQ$^{\bullet}$)$AlCl_2$, and we believe that the two ESR-active contributors to the spectrum in Fig. 4(a) are (p-SQ$^{\bullet}$)$AlCl_2$ and [(p-SQ$^{\bullet}$)ClAl(μ-Cl)$_2$$AlCl_2$($p$-Q)]. Complexation of this type is more likely than the formation of [(p-SQ$^{\bullet}$)$AlCl_2$]$_2$ dimers, since the concentration of (p-Q)$AlCl_3$ is much higher than that of the semiquinone derivative. In keeping with this, no half-field resonance was detected in either of the systems in question, indicating the absence of diradical species in solution.





Solutions of (p-$C_6X_4O_2$)AlX_3 (X = Cl or Br), and of the corresponding 1,4-naphthoquinone adduct, gave weak broad ESR spectra in the region of $g = 2$, but it was not possible to extract any quantitative information from these results.

Adducts with *ortho*-quinones

Stable 1 : 1 adducts were obtained by the reaction of $AlCl_3$ with three *o*-quinones (see Table 1), although the compound with 9,10-phenanthrenequinone consistently gave poor analysis. In general their solid state properties are similar to those of the *p*-quinone derivatives. There are small ($\approx$10–15 cm^{-1}) changes in the ν(C=O) region of the infrared spectrum, but no C–O modes were detected, in contrast to compounds in which *o*-semiquinones are present.[19] We conclude that these compounds are donor–acceptor adducts, whose colours are compatible with charge transfer from the ligand to metal centre.

The ESR spectra of adducts of *o*-quinone derivatives of Group III halides have been the subject of previous reports from this laboratory, and elsewhere.[1,20–22] In the case of tin(IV) halides, the structure of a 1 : 1 stable adduct of $SnCl_4$ with 1,10-phenanthrenequinone has been established by X-ray crystallography, which demonstrated also the formation of a six-coordinate complex with a $SnCl_4O_2$ kernel.[23] We suggest that adducts of *o*-quinones with $AlCl_3$ are the related five-co-ordinate analogues. In contrast, indium(III) halides react with *o*-quinones to give the corresponding (SQ$^{\bullet}$)InX_2 compounds (SQ = semiquinonate; X = Cl or I), whose ESR spectra have been analysed. Crystallographic analysis of the derivative (dbbsq$^{\bullet}$) InI_2(pic)$_2$ (dbbsq$^{\bullet}$ = 3,5-di-*tert*-butyl-*o*-benzosemiquinonate anion; pic = 4-methylpyridine) confirmed the presence of the semiquinonate ligand in this six-co-ordinate indium(III) complex.[2,24]

As in the case of the *p*-quinone adducts discussed above, weak ESR activity was detected from solid samples of the *o*-quinone derivatives, and this is again believed to be due to impurities. Solutions of these compounds show much more intense spectra. In the case of (dbbq)$AlCl_3$ (Table 1, sample 9), the spectrum of a dilute solution in toluene showed hyperfine coupling to aluminium (^{27}Al, $S = 5/2$) and one proton of the semiquinone ligand; the only parameters which could be derived from the rather broad signals were $g \approx 2.0$, $A_{Al} = 2.4$ G, $A_H = 2.9$ G (1H). Abakumov and Klimov[21] studied this system some years ago, and reported $A_{Al} = 2.2$ G, $A_H = 4.4$ G. The reason for the difference is not clear, but in general our values are closer to those derived for other aluminium(III) species in this work, and with those reported earlier by us for other dbbsq$^{\bullet -}$ complexes.[2] For the phenanthrenequinone adduct our values for a dilute solution in toluene, $g = 2.0037$, $A_{Al} = 2.35$ G, $A_H = 2.2$ (4H), 0.5 G (4H), are in agreement with those found for this species in diglyme (2,5,8-trioxanonane) or tetrahydrofuran ($A_{Al} = 2.05$, $A_H = 2.0$ (4H), 0.45 G (4H)),[22] taking into account the different solvents used.

We conclude, with previous workers,[22] that the *o*-quinone adducts of $AlCl_3$ are stable five-co-ordinate species in the solid state, but that in organic solvents decomposition results from the intramolecular electron transfer described in eqn. (1). The present work suggests that the behaviour of *o*- and *p*-quinone adducts is essentially identical in terms of electron transfer and decomposition, but that there are differences in the subsequent solution chemistry inherent in the different co-ordinating properties of mono- and bi-dentate ligands.

Acknowledgements

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