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The reactions of elemental germanium with 3,5-di-*tert*-butyl-1,2-benzoquinone

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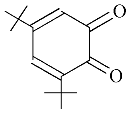
Germanium powder reacts slowly with 3,5-di-*tert*-butyl-1,2-benzoquinone (dbbq) in refluxing toluene to give products whose composition depends on the initial mole ratio of the reactants. When Ge : dbbsq = 1 : 2, the solid product is a monoradical + diradical species, but in non-aqueous solvents this converts to a diamagnetic oligomer. Treatment with 2,2′-bipyridine, or monodentate nitrogen donors (= L) gives diamagnetic germanium(IV) derivatives $Ge(dbc)_2L_2$ (dbc^{2-} = 3,5-di-*tert*-butylcatecholate dianion). When the initial Ge : dbbq mole ratio = 1 : 3, the product is the diradical $Ge(dbbsq^{\bullet})_2(dbc)$. The reaction of Ge and 4 dbbq, or the treatment of GeX_4 (X = Cl, Br) with 4 moles of $Na(dbbsq^{\bullet})$, gives a product identified as $Ge(dbbsq^{\bullet})_2(dbc)(dbbq)$, but the structure of this compound is unclear. The solid state and solution properties of these unusual compounds are discussed in the light of ^1H NMR and electron spin resonance (ESR) spectroscopy.

Introduction

The mechanism of electron transfer in the redox reactions of Main Group elements and their compounds, has been the subject of a number of publications from this laboratory.[1–4] The most important general conclusion, based on both preparative and spectroscopic investigations, is that processes which were earlier believed to involve the concerted transfer of a pair of electrons in fact proceed *via* successive single-electron transfers. We have also demonstrated that intermolecular electron transfer can be a significant factor in such systems. The present work extends these studies by examining the preparation and spectroscopic behaviour of the various species which are obtained from the reactions of elemental germanium with 3,5-di-*tert*-butyl-1,2-benzoquinone (dbbq) in differing mole ratios. The study of these products also underlines the importance of coordination chemistry in understanding both intermolecular transfer processes, and the structural relation between solid state and solution phase species.



dbbq

Experimental

Germanium pieces, Br_2, $GeCl_4$, pyridine (py), 4-methylpyridine (pic), 4-*tert*-butylpyridine (Bupy), and 2,2′-bipyridine (bpy) and dbbq were used as received (Aldrich). $GeBr_4$ was prepared by following an earlier procedure in which Ge (1.45 g, 2 mmol) and Br_2 (1.28 g, 8 mmol) were reacted in refluxing perfluorodecalin (25 cm^3).[5] Solvents were dried by standard methods and stored over appropriate drying agents. All preparative work was carried out in an atmosphere of dry nitrogen.

Germanium was estimated gravimetrically by precipitation with tannic acid and ignition at 1000 °C to germanium(IV) oxide.[6] Microanalysis was performed by Canadian Microanalytical Service Ltd. Infrared spectra were run as KBr discs on a Bowmem 100 instrument over the range 4000–400 cm^{-1}; ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300L instrument, and electron spin resonance (ESR) spectra on a Bruker ESP-300E spectrometer, using the calibration and other methods described earlier.[7] Mass spectra were recorded on a Kratos Profile high-resolution double focussing spectrometer operating in the electron impact (EI) mode. UV–VIS spectra of solutions were obtained on a Cary 50 instrument.

In this paper we follow earlier practice by using the nomenclature dbbq, $dbbsq^{\bullet-}$ and dbc^{2-} for the quinone, semiquinonate anion and *o*-diolato forms of 3,5-di-*tert*-butyl-1,2-benzoquinone, and we write the formulae as GeQ_n in those situations in which the structure of the ligands is in question.

Reaction between Ge and dbbq, 1 : 2

Germanium (0.2 g, 2.75 mmol) was added to a solution of dbbq (1.22 g, 5.5 mmol) in toluene (30 cm^3). No reaction was detected at room temperature, but under reflux the red colour of the solution changed slowly, gradually becoming green–blue after *ca.* 10 h; the progress of the reaction was difficult to follow, given the intense colours involved, but the rate is clearly low, and we found that a period of 12 d under reflux was needed to give optimum yields. The final solution was filtered to remove any traces of unreacted germanium, and solvent was evaporated *in vacuo* to give a free flowing blue–green powder, GeQ_2, obtained in essentially quantitative yield. Analytical results for this, and other products, are given in Table 1. The infrared spectrum of the solid showed the absence of ν(C=O), found as a strong feature at 1660 cm^{-1} in the spectrum of dbbq. The ESR spectrum of this material, discussed in detail below, shows that it contains a diradical; the spectroscopic properties of solutions of this compound are also discussed below. The mass spectrum had a multiplet centered at $m/z = 514$, corresponding to the molecular ion, and this is a significant feature of the mass spectra of other compounds prepared in these studies.

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Table 1 Analytical results, with calculated values in parentheses, for germanium derivatives of dbbq

			Analysis (%)			
Product	Colour	Mp/°C	Ge	C	H	N
GeQ_2	Blue–green	85	14.1(14.2)	65.2(65.5)	7.90(7.80)	—
$Ge(dbc)_2(bpy)$	Brown	170	10.7(10.9)	68.2(68.2)	7.00(7.15)	4.12(4.18)
$Ge(dbc)_2(py)_2$	Brown	140	11.1(10.9)	—	—	—
$Ge(dbc)_2(pic)_2$	Mustard yellow	100	10.4(10.4)	68.7(68.7)	7.75(7.70)	3.95(4.00)
$Ge(dbc)_2(Bupy)_2$	Pale brown	90	9.20(9.27)	70.8(70.5)	8.35(8.45)	3.42(3.57)
$Ge(dbc)_2(dmso)_2$	Brown	120	11.1(10.9)	58.0(57.4)	7.80(7.80)	—
GeQ_3	Blue	100	9.80(9.90)	68.2(68.8)	8.10(8.25)	—
GeQ_4	Green–blue	110	7.52(7.62)	70.5(70.2)	8.70(8.40)	—
$Ge(dbc)_2(dbbq)(pic)$	Pale brown	90	8.87(8.94)	69.0(69.5)	8.10(8.00)	1.68(1.72)
$Ge(dbc)_2(dbbq)(pic)$	Mustard yellow	80	8.60(8.71)	69.8(69.7)	8.40(8.25)	1.58(1.69)
$Ge(dbc)_2(dbbq)(Bupy)$	Pale brown	100	8.40(8.36)	70.8(70.5)	8.60(8.40)	1.70(1.60)

Reaction of GeQ_2 with nitrogen donors

(i) 2,2-Bipyridine. When GeQ_2 was treated with an equimolar quantity of bpy in toluene (30 cm^3), the colour of the solution immediately changed to brown, and a brown solid separated. This diamagnetic material was identified as the germanium(IV)-biscatecholate derivative $Ge(dbc)_2(bpy)$. The infrared spectrum included peaks at 3022 (aromatic γCH), 1691(bpy), 1260(bpy), 660 cm^{-1} (pyridine ring vibrations); ^1H NMR (CD_3CN): δ 8.81 (d, 2H, $J = 4.3$), 8.45 (d, 2H, $J = 7.02$), 8.26 (t, 2H, $J = 7.0$), 7.72, (t, 2H, $J = 4.97$ Hz), 6.02 (m) and 1.23, 1.45 (m, 36H).

(ii) Py, pic, Bypy (=L). Similar reactions with a ten-fold excess of these ligands at room temperature gave the products $Ge(dbc)_2L_2$, all of which are stable yellow–brown solids, and none of which show any ESR activity.

Reaction between Ge and dbbq, 1 : 3

Other than the quantity of dbbq, the procedures were those described above, as was the course of the reaction and the isolation of GeQ_3 as a green–blue powder in high yield. Infrared spectroscopy showed the absence of ν(C=O) in this product. The ESR spectrum of the solid (see below) showed that this compound is a diradical, formulated as $Ge^{IV}(dbbsq^{\bullet})_2(dbc)$.

A solution of GeQ_2 and an equivalent quantity of dbbq in toluene was refluxed for 10 h; the resultant blue–green solution was evaporated to dryness, to give a solid whose IR spectrum was identical with that of a sample of GeQ_3 prepared by the methods described above.

Reaction between Ge and dbbq, 1 : 4

The reaction between Ge and a solution containing 4 equivalents of dbbq shows the same features as those described above. The solid product, which analyzed as GeQ_4, was obtained in almost quantitative yield as a blue–green powder, and showed strong ν(C=O) features in the infrared spectrum. The ^1H NMR spectrum in CD_3CN has broad features, and the ESR spectrum is that of a diradical. These properties are compatible with the solid state structure $Ge^{IV}(dbbsq^{\bullet})_2(dbc)(dbbq)$; the implications of this are discussed below.

As in the treatment of GeQ_2 with dbbq noted above, we found that the reaction of GeQ_2 with 2 equivalents of dbbq yielded the green solid GeQ_4 after refluxing and evaporation.

Reaction of GeQ_4 with N-donors

The addition of a ten-fold excess of pyridine, picoline or 3-butylpyridine (= L) to a solution of GeQ_4 in toluene produced a red reaction mixture; this change in colour is ascribed to the release of dbbq. Partial removal of solvent, and cooling, produced yellow–brown solids containing Ge : Q : L in the ratio 1 : 3 : 1. These solids are ESR-silent; a solution in toluene shows a biradical spectrum, but the frozen solutions have no ESR activity. The ^1H NMR spectra ($CDCl_3$, CD_3CN) have only broad features, but are better resolved than in the case of the GeQ_4 starting material. We found no evidence of a reaction between GeQ_4 and 2,2′-bipyridine.

Reaction of GeX_4 (X = Cl, Br) with $Na^+(dbbsq^{\bullet})^-$

The treatment of H_2dbc (1.85 g, 8.3 mmol) in toluene (30 cm^3) with NaH (0.2 g, 8.3 mmol) gave a blue solution of $Na^+(dbbsq^{\bullet})^-$, to which $GeCl_4$ (0.45 g, 2.08 mmol) or $GeBr_4$ (0.82 g, 2.08 mmol) in the same solvent (10 cm^3) was added dropwise. The reaction mixture, which immediately became green, was stirred for 4 h at room temp., after which the precipitated NaX was collected by filtration. The yield was almost quantitative (97%) in each case. The filtrate was concentrated to give a blue–green solid which was shown to contain no halide, and which was analytically and spectroscopically identical with the material obtained from the reaction of Ge with 4 equivalents of dbbq (see above).

Cyclic voltammetry

Cyclic voltammograms were recorded on a three-electrode potentiostat (BAS Model CV-27) coupled to a Houston Model 100 recorder. The cell was fitted with a working platinum disc electrode (BHS Model, area 0.022 cm^2), a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode, which was separated from the main compartment by a porous ceramic disk. Solutions were deoxygenated with a stream of dry nitrogen for 15 min before making measurements.

Results and discussion

The GeQ_2 system

The oxidation of elemental germanium by dbbq can be discussed in the light of the reaction of this orthoquinone with alkaline-earth metals,[3] with gallium, indium and thallium, and with tellurium.[8–11] With the exception of the last element, the primary products are the appropriate semiquinonate derivatives; tellurium gives the catecholate $Te(dbc)_2$. We establish below that the product GeQ_2 is a diradical in the solid state, but goes to a diamagnetic species in solution in aromatic solvents. Prokof'ev *et al.*[12] have reported the preparation of a diradical $Ge(3,6\text{-}sq^{\bullet})_2$ ($sq^{\bullet -}$ = 3,6-di-*tert*-butyl-1,2-benzoquinone radical anion), but do not appear to have detected the change in magnetic properties on dissolution.

Before reviewing the structural and spectroscopic results for the germanium systems, we note that the rate of reaction here is significantly less than that found with other Main Group elements, for which a period of 24 h under reflux in toluene is sufficient for complete reaction. The reasons for this low rate are not obvious; we were careful to select shiny pieces of germanium, but it is still possible that a surface layer of oxide was present and that this inhibited the reaction with dbbq. We

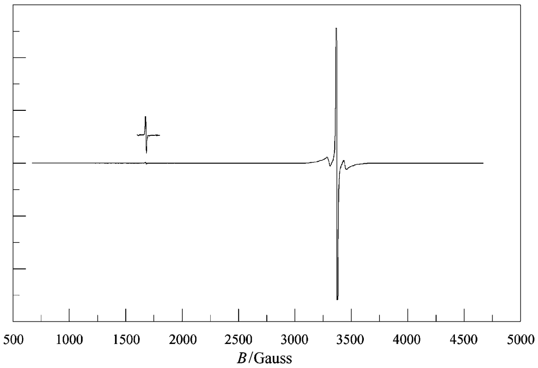


Fig. 1 ESR spectrum of solid GeQ_2 at 77 K, showing half-field resonance.

also found a major difference in the reaction of this element with tetrahalogenoorthoquinones ($X_4C_6O_2$; X = Cl, Br), compared to other main group elements, for which the reactions are generally similar to those with dbbq, but with germanium there is clear evidence of reaction at the C–X bonds. This will be discussed elsewhere.

The reaction mixture obtained from Ge + 2 dbbq after long reflux is dark green, and removal of solvent gives a blue–green powder. The ESR spectrum of this solid (Fig. 1) shows a resonance at half-field, demonstrating the presence of a diradical species, and this is confirmed by the zero-field spectrum. No resonance was detected at one-third field, but there is a strong sharp resonance at $g = 2.008$, indicating that a monoradical is also present. Careful integration of the relative intensities, taking into account the fact that there are two transitions in the $S = 1$ system, and that each transition has an intrinsic intensity twice as large as that for $S = \frac{1}{2}$, established that there are almost exactly two molecules with $S = \frac{1}{2}$ for every $S = 1$ species in this solid. Even after this procedure, the simulation of the spectrum is not completely satisfactory, implying the presence of other spin–spin interactions in the solid. In contrast, no ESR signal could be detected for a solution in toluene over a range of temperatures, including the frozen solution at 77 K.

In benzene (C_6D_6) solution, the ^1H NMR spectrum of GeQ_2 is sharp but complex in both the aliphatic and aromatic region, and the spectrum shows only slight changes over the temperature range 5–80 °C. The aliphatic region has four strong resonances (δ 1.71, 1.68, 1.41 and 1.24) of equal intensity, and a large number (*ca.* 15) of less intense resonances in the region δ 1.0–1.8. For comparison, 3,5-di-*tert*-butylcatechol has resonances at δ 1.64 and 1.38, and the parent *o*-quinone has the corresponding features at δ 1.24 and 0.85 (in C_6D_6), all readily assigned to *t*-C_4H_9. The sharp resonances in GeQ_2 are in keeping with the absence of ESR activity, and we conclude in the first place that the GeQ_2 unit present in aromatic solvents is the germanium(iv) derivative Ge(dbc)$_2$.

The structure of a species with a Ge(OO′)$_2$ core is an interesting problem. The bite angle in catecholate complexes is typically *ca.* 80 °C, and a pseudo-tetrahedral Ge(dbc)$_2$ monomer would therefore require severe distortion. Furthermore, such a monomer should only have two *t*-C_4H_9 ^1H NMR resonances, but oligomerisation through intermolecular O→Ge bonding from one oxygen of a catecholate ligand could produce units with trigonal-bipyramidal stereochemistry; which then makes all four *t*-C_4H_9 groups of the initial monomer different, thus explaining the ^1H NMR results (see above). A trimer [Ge(cat)$_2$]$_3$ **A** can be constructed on this basis, but no doubt higher order species can also exist, in keeping with the large number of *t*-C_4H_9 resonances observed; these could involve Ge(cat)$_2$ aggregates with six-coordinate germanium cores. Examination of models suggests that a dimeric structure would be unstable.

The UV–VIS spectrum of a solution [Fig. 2(a)] consists of a broad absorption, centered at 640 nm, and a weaker band at 420 nm. There is no structural information to be drawn from this of itself (but see below). The overall conclusion of all these spectroscopic results, is that in non-polar solvents, the solute is Ge(cat)$_2$, present as a mixture of oligomeric diamagnetic units.

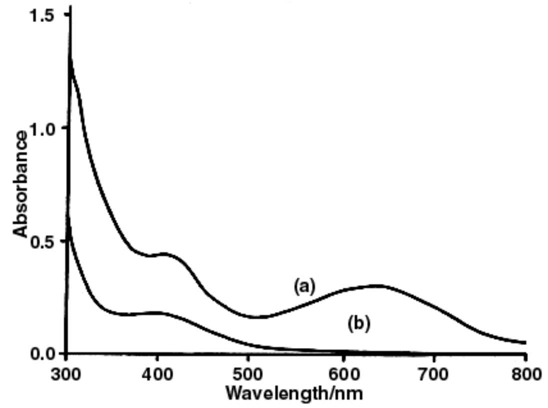
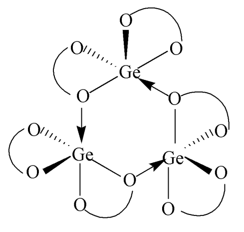
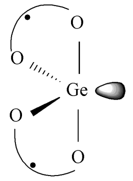


Fig. 2 UV–VIS spectra of GeQ_2 (a) in toluene and (b) in a toluene–dmso mixture.



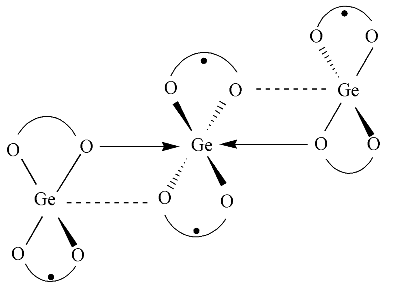
A

It is clear that precipitation of GeQ_2 from toluene solution causes drastic structural changes, as evidenced by the ESR results. The solid contains a diradical species, and perhaps the simplest such molecule which can be derived from Ge(dbc)$_2$ by intramolecular electron transfer is the germanium(ii) bis(semiquinonate) Ge(dbbsq$^•$)$_2$ **B**.



The stereochemistry shown follows that of Te($O_2C_6H_4$-*o*)$_2$, for which the trigonal-bipyramidal (AX_4E) structure has been established by X-ray crystallography,[13] although NMR studies of Te(dbc)$_2$ in $CDCl_3$ showed fluxionality in solution.[11] The crystal structure of Te($O_2C_6H_4$-*o*)$_2$ also identified significant intermolecular interactions in the solid state, with rows of ···O–TeO$_3$···O–TeO$_3$··· running through the lattice, so that the coordination of tellurium is distorted Te(OO′)$_2$O″E, where E represents the lone pair. The *D* value given for GeQ_2 in Table 2 (155 G) is in the order (150–250 G) reported earlier for a range of M(dbbsq$^•$)$_2$L$_n$ complexes (L = pyridine, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, 2,2′-bipyridine), but lower than in (say) the presumably *cis*-complexes M(dbbsq$^•$)$_2$(bpy) (M = Mg, *D* = 193 G; M = Zn, *D* = 202, 236 G).[3]

In addition, the powder of GeQ_2 demonstrably contains monoradical species, and there is also evidence of other weaker unresolved spin–spin interactions. Given the absence of crystalline material, and hence of X-ray structural data, any proposed structure must rely on the ESR results for the solid, and on the suggested solute species in toluene. The loss of one O→Ge bond in trimer **A**, followed by intramolecular electron transfer could lead to species **C** in which a [Ge^{IV}(dbbsq$^•$)]$^{2+}$ is linked by O→Ge bonding through the catecholate moieties of two [Ge^{II}-

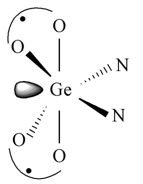


C

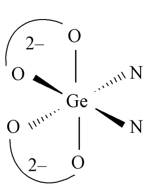
$(\mathrm{dbbsq}^{\bullet})(\mathrm{dbc})]^{-}$ groups. A trimer involving donation of the lone pairs of each $\mathrm{Ge^{II}}$ centre to $\mathrm{Ge^{IV}}$ can also be constructed; in either case, the diradical $\mathrm{Ge^{IV}(dbbsq^{\bullet})_2}$ group functions as an electron-pair acceptor from monoradical germanium(II) units, and the mean oxidation state of germanium is $2\frac{2}{3}$.

GeQ_2 and neutral donors

The treatment of a solution of GeQ_2 in toluene with excess 2,2′-bipyridine, or with monodentate nitrogen donors [pyridine, picoline, 4-butylpyridine (= L)], causes an immediate colour change. The solid products which are isolated from the resultant brown–yellow solutions are ESR-silent, and are characterised by ^{1}H NMR spectra with sharp well defined features, and are formulated as adducts of germanium(IV)-bis(3,5-di-*tert*-butylcatecholate), with the stoichiometries $\mathrm{Ge(dbc)_2(bpy)}$ and $\mathrm{Ge(dbc)_2L_2}$. Related six-coordinate germanium(IV) complexes were prepared some time ago by Yoder and Zuckerman[14] by the reaction between $\mathrm{GeCl_4} + 2\ \mathrm{C_6H_4(OH)_2}$-1,2 in pyridine, yielding $\mathrm{Ge(O_2C_6H_4)_2(py)_2}$, and related products. These $\mathrm{Ge(dbc)_2L_2}$ molecules are best regarded as being structurally related to the solute oligomers $[\mathrm{Ge(dbc)_2}]_n$, but the relationship to the radical solid state species can equally be understood, in terms of the coordination chemistry. The addition of a bidentate donor, or two monodentate donors, to the five-coordinate species **B** presents two possibilities, species **D** and **E**,



D



E

one product being a seven-coordinate germanium(II) species, and the other the six-coordinate germanium(IV) bis-catecholate adduct actually found. The transformation to the latter structure would involve intramolecular electron transfer from germanium to ligand, and can be written by eqn. (1),

$$\mathrm{Ge^{II}} + 2\ \mathrm{dbbsq}^{\bullet -} \xrightarrow{\mathrm{L}} \mathrm{Ge^{IV}} + 2\ \mathrm{dbc}^{2-} \qquad (1)$$

the reaction being driven by the presence of the donor L, and the consequent stabilization induced by six-coordination.

Solutions of GeQ_2 in dimethyl sulfoxide, ethanol, or acetonitrile are brown, and contain diamagnetic species, as evidenced by the sharp NMR resonances at room temperature, and we identify these solutes as $\mathrm{Ge(dbc)_2(solv)_2}$ (solv = dmso, EtOH, MeCN) by analogy with the nitrogen donor derivatives described above. In the case of dmso, this was confirmed by evaporating the solution to give a brown powder analysing as $\mathrm{Ge(dbc)_2(dmso)_2}$ (see Table 1); with ethanol, in contrast, evaporation of the brown solution yielded the blue–green GeQ_2 starting material. The UV-visible spectrum of GeQ_2 in a toluene–dmso mixture [Fig. 2(b)] shows significant changes from that in pure toluene, notably in the absence of the feature at 640 nm, in qualitative agreement with a marked structural change.

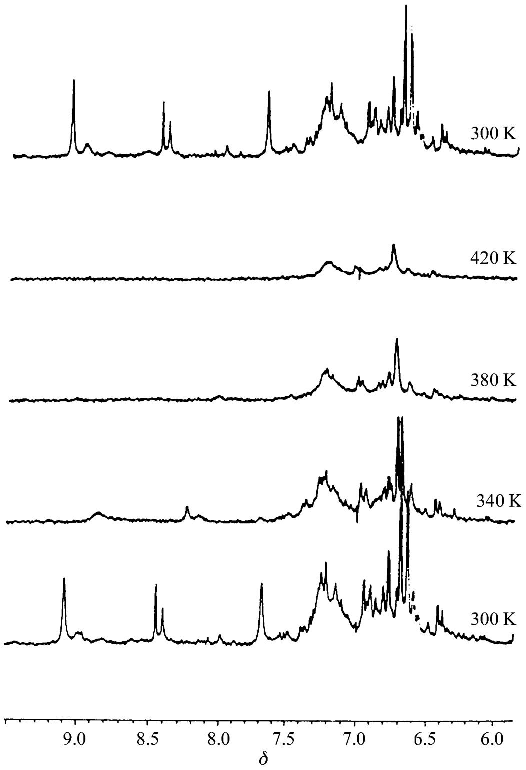


Fig. 3 ^{1}H NMR spectrum of GeQ_2 in $(CD_3)_2SO$ over the temperature range 300–420 K.

In $(CD_3)_2SO$, the ^{1}H NMR spectrum shows an interesting reversible temperature dependence over the range 300–420 K (Fig. 3). At the lowest temperature, there are strong resonances in the region δ 8.0–9.5, but with increasing temperature these broaden and move to higher field, until at 420 K the whole spectrum has lost most of the definition; cooling to 300 K reverses these changes. These results indicate the generation of paramagnetic species in solution; a possible mechanism involves loss of dmso to give a monosolvate [eqn. (2)] followed

$$\mathrm{Ge(dbc)_2(dmso)_2} \rightleftharpoons \mathrm{Ge(dbc)_2(dmso)} + \mathrm{dmso} \qquad (2)$$

by intramolecular electron transfer to give a six-coordinate germanium(II) species [eqn. (3)]

$$\mathrm{Ge(dbc)_2(dmso)} \rightleftharpoons \mathrm{Ge^{II}(dbbsq^{\bullet})_2(dmso)E} \qquad (3)$$

where E is the lone pair of electrons on germanium. Solutions of GeQ_2 in dmso show a weak reproducible ESR activity, in agreement with eqn. (3). No resonance could be detected at the half-field, but in view of the weakness of the resonance at $g = 2.0068$, this is not surprising, and certainly not diagnostic. Solutions of GeQ_2 in CD_3CN, and of $\mathrm{Ge(dbc)(py)_2}$ in $CHCl_3$ show no such effects according to ^{1}H NMR spectroscopy at room temperature; presumably stronger coordination by these nitrogen donors inhibits eqn. (2), and hence eqn. (3).

The GeQ_3 system

The solid product of the reaction of Ge + 3 dbbq in refluxing toluene is analytically GeQ_3, and this same product can be produced, not surprisingly, by the oxidation of GeQ by an equimolar quantity of dbbq in refluxing toluene. Prokof’ev *et al.*[12] also found that $\mathrm{Ge(3,6\text{-}sq^{\bullet})_2}$ reacted with excess ortho-quinone to give a diradical, which they formulate as Ge(3,6-

Table 2 Spin Hamiltonian parameters for $S = 1$ systems

Compound	g	D/G	E/G
$\mathrm{GeQ_2}$ (powder)	2.008	155	7
$\mathrm{GeQ_3}$ (powder)	2.007	175	10
$\mathrm{GeQ_4}$ (frozen solution)	2.007	260	22

$\mathrm{sq^{\bullet})_2(3,6\text{-}q)}$, but which in the light of our results we suggest is $\mathrm{Ge(3,6\text{-}sq^{\bullet})_2(3,6\text{-}cat)}$. A similar $\mathrm{M^{II}{\rightarrow}M^{IV}}$ oxidation has also been found by this group for the tin derivatives of 3,6-di-*tert*-butyl-1,2-benzoquinone.[15]

The ESR spectrum of $\mathrm{GeQ_3}$ in the solid state is almost identical to that shown in Fig. 1, but the simulation is much better (see Table 2) and there is no evidence of other spin–spin interactions. These results, and the absence of ν(C=O) in the infrared spectrum, identify the solid as the mononuclear six-coordinate germanium(IV) complex $\mathrm{Ge(dbbsq^{\bullet})_2(dbc)}$. The reaction sequence here, and in the $\mathrm{GeQ_2}$ system discussed above, requires the oxidation of elemental germanium to $\mathrm{Ge^{II}(dbbsq^{\bullet})_2}$, which in the absence of other reagents undergoes metal→ligand electron transfer to give $\mathrm{Ge^{IV}(dbc)_2}$. Excess orthoquinone can bring about a process similar to that involving 2,2′-bipyridine and other neutral donors (see above) [eqn. (4)].

$$\mathrm{Ge^{II}(dbbsq^{\bullet})_2 + dbbq \longrightarrow Ge^{IV}(dbc)_2(dbbq)} \tag{4}$$

Intramolecular electron transfer can then occur between two ligands [eqn. (5)] by a process which parallels the known solution reaction [eqn. (6)].

$$\mathrm{Ge(dbc)_2(dbbq) \rightleftharpoons Ge(dbbsq^{\bullet})_2(dbc)} \tag{5}$$

$$\mathrm{dbbq + dbc^{2-} \rightleftharpoons 2\ dbbsq^{\bullet -}} \tag{6}$$

A similar intramolecular process was detected[8,10] in the gallium(III) complex $\mathrm{Ga(dbbsq^{\bullet})_3}$, and identified as equilibrium (7) so that there is a reasonable parallel in the behaviour of these related gallium(III) and germanium(IV) species.

$$\mathrm{Ga(dbbsq^{\bullet})_3 \rightleftharpoons Ga(dbbsq^{\bullet})(dbq)(dbbq)} \tag{7}$$

Solutions of $\mathrm{GeQ_3}$ in toluene show no ESR activity, establishing that here, as with $\mathrm{GeQ_2}$, there are significant electronic differences between solid and solution. The most probable explanation is the reversal of eqn. (5) to give $\mathrm{Ge(dbc)_2(dbbq)}$, and the formation of oligomers, as discussed above for $\mathrm{GeQ_2}$.

Germanium + 4 dbbq, and $\mathrm{GeX_4 + 4\ Na^+(dbbsq^{\bullet -})}$

The oxidation of germanium in refluxing toluene by a four-fold excess of dbbq gave, as in the case of the reactions discussed above, a green powder. Elemental analysis showed a Ge : Q ratio of 1 : 4; in agreement with the almost quantitative yield of product and the complete consumption of germanium. As with $\mathrm{GeQ_3}$, the ^{1}H NMR of this material showed only broad features, and the ESR spectrum of a dilute solution established the presence of a diradical. The infrared spectrum has a strong absorption at 1659 cm^{-1}, indicating that the solid contains orthoquinone; we return to this below.

The essential features of the reaction between $\mathrm{GeX_4}$ and 4 equivalents of $\mathrm{Na^+(dbbsq^{\bullet -})}$ are the same as those previously observed in similar metatheses, namely the quantitative precipitation of NaX, and the formation of a multi-radical derivative.[10,16,17] In the present work, the germanium product is identical with that obtained from the reaction Ge + 4 dbbq, so that the reaction sequence is presumably given by eqns. (8)–(10).

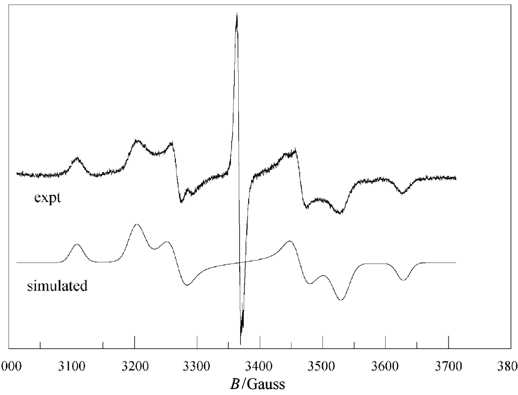


Fig. 4 ESR spectrum of $\mathrm{GeQ_4}$; frozen solution in toluene, 77 K.

$$\mathrm{GeX_4 + 4\ Na(dbbsq^{\bullet}) \longrightarrow Ge(dbbsq)_4 + 4\ NaX} \tag{8}$$

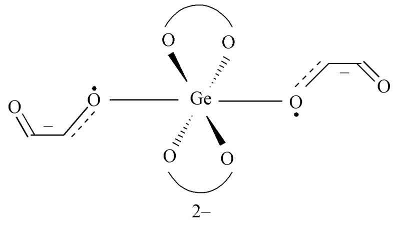
$$\mathrm{Ge(dbbsq)_4 \longrightarrow Ge(dbbsq^{\bullet})_2(dbc)(dbbq)} \tag{9}$$

$$\mathrm{2\ dbbsq^{\bullet -} \rightleftharpoons dbc^{2-} + dbbq} \tag{10}$$

The essential process [eqn. (10)] in the rearrangement in eqn. (9) is the reverse of eqn. (6) so that the preferred direction of this process depends, not unreasonably, on the specific reaction conditions, and on the coordination state.

Formulation of this $\mathrm{GeQ_4}$ complex, in either the solid state or non-aqueous solution, is difficult. The solid contains the orthoquinone, as established by the infrared spectrum, and the ESR spectrum (Fig. 4) demonstrates the presence of a diradical at room temperature and at 77 K. One possibility is an eight-coordinate species $\mathrm{Ge(dbbsq^{\bullet})_2(dbc)(dbbq)}$. Evidence for such oxy-ligand coordination is lacking, and a pseudo-cubane structure seems unlikely, given the constraints imposed by the bite angle of the ligands (see above). A pseudo-tetrahedral packing of ligands around a germanium(IV) centre is another possibility, as is a six-coordinate complex in which both semiquinonate ligands are monodentate.

The ESR spectrum of a solution of $\mathrm{GeQ_4}$ in toluene is also that of a diradical, and Fig. 4 shows both zero-field splitting and a half-field resonance in the spectrum of a frozen solution at 77 K. The D and E parameters, 260 and 22 G respectively, are significantly different from those for $\mathrm{GeQ_3}$ (see Table 2), and the D value in particular implies that the free electron sites are further apart in $\mathrm{GeQ_3}$ than in $\mathrm{GeQ_4}$, at least in solution. Substantial distortion from axial symmetry is demonstrated by the E-value. The spectrum also establishes the presence of a second $S = 1$ species, with $D \approx 205$ G, and of a monoradical ($g = 2.0078$); the intensity of this resonance is < 10% of the total spectrum in Fig. 4. A scheme which provides some explanation of these solid and solution spectra depends on the proposed monodentate $\mathrm{dbbsq^{\bullet -}}$ ligands shown in **F**. Such a species could indeed have the radical centres closer together in solution than in $\mathrm{Ge(dbbsq^{\bullet})_2(dbc)}$, and would be axially-distorted from octrahedral symmetry. Both *cis*- and *trans*-isomers of the $\mathrm{GeQ_4}$ species are possible, thereby leading to two different diradical



F

Table 3 Electrochemical results[a]

Compound	$E_a(1)$	$E_a(2)$	$E_a(3)$
GeQ_2	1.27	1.55	—
Ge(dbc)$_2$(bpy)	0.85	1.20	1.50
GeQ_4	1.28	1.56	—
GeQ_3(pic)	0.80	1.37	1.60
GeQ_3(Bupy)	0.80	1.42	1.62

[a] Solutions in acetonitrile, conc. 1–3.1 mM, containing 0.1 M tetrabutylammonium hexafluorophosphate, at room temperature. Potentials in V, *vs.* Ag/AgCl.

spectra, as observed, and dissociation [eqn. (11)] would give contributions from monoradical species.

$$\mathrm{Ge(dbbsq^{\bullet})_2(dbc)(dbbq)} \rightleftharpoons \mathrm{[Ge(dbbsq^{\bullet})(dbc)(dbbq)]^{+} + dbbsq^{\bullet -}} \quad (11)$$

We can also report that an ESR spectrum run some months after the original experiments showed no ESR activity, suggesting a slow decomposition of GeQ_4 in solution, so that the mono-, and the second diradical, components of Fig. 4 may arise from decomposition products.

Reaction of GeQ_4 with nitrogen donors

We found no evidence of any reaction between GeQ_4 and 2,2′-bipyridine, but the compound does react readily with monodentate nitrogen donors in toluene, giving a red solution and insoluble yellow–brown solid products. The former observation suggests the release of dbbq, and the yellow–brown solid products are found to be adducts of pyridine, picoline, or 4-butylpyridine of the general formula GeQ_3L. As noted, these solids are ESR-silent and examination of the infrared spectra, and in particular comparison with the spectra of the corresponding Ge(dbc)$_2$L$_2$ compounds, establishes the presence of ν(C=O), and hence of dbbq, in these unusual adducts. The ESR spectrum of a solution in toluene at room temperature is again identical with that of Ge(dbbsq$^{\bullet}$)$_2$(dbc) suggesting that in solution dissociation of the ligand is followed by intramolecular electron transfer, which can be written as eqn. (12)

$$\mathrm{Ge(dbc)_2(dbbq)L} \rightleftharpoons \mathrm{Ge(dbbsq^{\bullet})_2(dbc) + L} \quad (12)$$

with the inter-ligand electron transfer identified as that in eqn. (6). A frozen solution at 77 K showed no ESR resonance, so that eqn. (12) lies strongly to the left at low temperatures.

The absence of suitable crystals means that it has not been possible to identify the structure of these Ge(dbc)$_2$(dbbq)L adducts by X-ray crystallography. A parallel can be drawn with the six- and seven-coordinate species **D** and **E**, in which the coordination of the electron-pair donating nitrogen ligands facilitates the conversion of dbbsq$^{\bullet -}$ to dbc^{2-} in the coordination sphere. This argument suggests that Ge(dbc)$_2$(dbbq)L may be weak seven-coordinate germanium(IV) complexes.

Electrochemical studies

Table 3 reports oxidation potentials obtained by cyclic voltammetry of dilute solutions of selected compounds in acetonitrile. Di-*tert*-butylcatechol (H$_2$dbc) does not undergo reduction under these conditions over the potential range studied (0–2.2 V), being already the most highly reduced state of the dbbq–dbbsq$^{\bullet -}$–dbc^{2-} triad, but can be oxidized at +1.36 V to [H$_2$dbc]$^{\bullet +}$, which undergoes rapid decomposition, as demonstrated by the absence of the cathodic peak. The parent orthoquinone shows the expected reversible reduction to dbbsq$^{\bullet -}$ and dbc^{2-}, with the respective potentials $E_c(1)$, $E_a(1) = -0.60$, -0.42 V and $E_c(2)$, $E_a(2) = -1.77$, -1.47 V; the current intensity for the second step is much lower than for the first, due to the disproportion process shown in eqn. (10), for which K is estimated at *ca.* 10^9.

The ratio of current to (sweep rate)$^{\frac{1}{2}}$ in the germanium systems discussed below was found to be constant over the range 0.1–0.4 V s^{-1}, which implies diffusion controlled processes in each case, within the limited range available for investigation. None of the systems studied (Table 3) showed primary reduction peaks. For GeQ_2, two oxidation steps were observed, with the second of these showing slight reversibility. In the light of the discussion of the NMR and ESR results above on the species present in basic solvents, the solute is identified as Ge(dbc)$_2$(MeCN)$_2$, and since dbc^{2-} is not reducible under these conditions (see above), we ascribe these processes to intramolecular electron transfer to the germanium(IV) centre [eqn. (13)]

$$\mathrm{Ge^{IV}(dbc)_2(solv)_2} \rightleftharpoons \mathrm{Ge^{III}(dbc)_2(solv)_2} \rightleftharpoons \mathrm{Ge^{II}(dbc)_2(solv)_2} \quad (13)$$

For the 2,2′-bipyridine adduct of Ge(cat)$_2$, the oxidation potentials are substantially different from those with GeQ_2, and clearly reflect the strong donation of electron density to the germanium centre, shown by the characteristic lowering of $E_a(1)$, and to a lesser extent of $E_a(2)$. In addition, a third process is seen, at 1.50 V, and this is assigned to irreversible oxidation of the nitrogen ligand. It was not possible to study the electrochemical behaviour of GeQ_2 in toluene, owing to the low solubility of supporting electrolytes, so that a comparison with the spectroscopic results for this solvent system is not available.

The behaviour of GeQ_4 in acetonitrile is essentially identical to that of GeQ_2 in the same solvent, implying that reduction at the germanium(IV) centre also occurs in this system. The last two results in Table 3 refer to adducts produced by the reaction of GeQ_4 with picoline and 4-butylpyridine; the potentials are similar to those for Ge(dbc)$_2$(bpy), suggesting that reduction of germanium(IV) occurs in these solutes, with a marked effect due to donation from the nitrogen ligands. Equally, the potentials assigned to the oxidation of these ligands are similar to those for 2,2′-bipyridine.

The CV results are thus in agreement with the ESR and NMR spectroscopic data, but beyond that do not help significantly in elucidating the structures of these species in solution.

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