Electron Spin Resonance Spectra and Conformations of Group 2 Ion Complexes with a Semidione Ligand

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The triplet states of the complexes formed between the semidione 1,1,4,4-tetramethyltetralin-2,3-dione and Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+} have been studied by e.s.r. spectroscopy in frozen solutions of 2-methyltetrahydrofuran. The e.s.r. spectrum of [Al(tmtd)$_3$] [tmtd = 1,1,4,4-tetramethyltetralin-2,3-dionate(1−)] has been attributed to a quartet state. The zero-field splitting parameters for the [M(tmtd)$_2$] complexes have been obtained and compared with those calculated by electron dipole–dipole interaction for a number of conformations of the complexes. The conformations giving the best fit are reported. The discrepancy between experimental and calculated zero-field splitting parameters for the complexes of Sr^{2+} and Ba^{2+} has been explained by an additional spin–orbit contribution.

RADICAL anions formed by the reaction of bivalent and trivalent metals in solvents of low dielectric constant with aromatic compounds may give rise to ionic aggregates such as triple or quadruple ions. A number of triple ions formed by a bivalent metal and two radical anions in a triplet state have been studied by e.s.r. spectroscopy.[1,2]

Rigid glass solutions provide e.s.r. spectra from which the zero-field splitting parameters D and E of the electron–electron dipolar interaction can be obtained. These parameters depend on the geometry of the ionic aggregate and on the radical anion spin-density distribution. When the latter is known, it is possible to compare the calculated zero-field splitting parameters for different geometries of the complex with the experimental ones. If the radical anion is a bidentate ligand, solvent molecules play a minor role in determining the molecular arrangement of the complex around the metal atom and possible geometries of the complex can be easily identified. Moreover, when the π system in the ligand is spread over only a few centres, a reliable spin-density distribution can be obtained by symmetry considerations and from the hyperfine coupling constants in the radical anions.

In this paper we report the details of an e.s.r. study on the complexes formed by the reduction with Zn, Be, Mg, Ca, Sr, Ba, and Al of the aliphatic dione, 1,1,4,4-tetramethyltetralin-2,3-dione,† whose radical anion has the unpaired electron spread over four atoms. The two-fold symmetry of the spin distribution allows the spin densities to be determined through the ^{13}C hyperfine coupling constants of the uniradical in liquid solution. Hence, a valuable correlation between the zero-field splitting parameters and the structure of the complex can be achieved.

EXPERIMENTAL

1,1,4,4-Tetramethyltetralin-2,3-dione was prepared by the method of Bruson *et al.*[3] from 2,5-dihydroxy-2,5-dimethylhex-3-yne (K. and K.).

The reduction to tmtd, with all metals but Be, was carried out by shaking a metal–mercury amalgam with a solution of the dione in 2-methyltetrahydrofuran *ca.* 10^{-2} mol dm^{-3} under vacuum. The solvent was purified and stored in the usual way.

The ion pair with Li was obtained by reduction under the same conditions with small pieces of the metal.

The [Be(tmtd)$_2$] complex was obtained by treating $BeCl_2$ with the tmtd uniradical obtained by reduction with a potassium mirror.[4]

RESULTS

The e.s.r. spectra of frozen 2-methyltetrahydrofuran solutions of the tmtd semidione complexes with the bivalent metals are typical of randomly oriented triplets.[5] Zero-field splitting parameters were obtained by computer simulation of the spectrum when a superposition of e.s.r. lines due to different complexes occurred, or simply by measuring distances between e.s.r. lines in the other cases. A typical spectrum with the corresponding simulation is shown in Figure 1. The results are collected in Tables 1 and 2.

Only one type of complex is formed with Be, Ba, and Zn, four types with Mg and Ca, and three with Sr; in most cases a non-vanishing E value was observed. A regular decrease in the zero-field splitting parameters with increasing ionic radius of the metal was observed, with the exception of the complexes of Sr^{2+} and Ba^{2+}. In fact, the D value of the latter complex is larger than that of the former (Table 2).

The complex with Al^{3+} exhibits an e.s.r. spectrum with similar features to those of bivalent metal complexes. However, the very large field separation between the outermost absorption peaks (712 G) that corresponds to $2D$ in a triplet-state spectrum suggests that the e.s.r. spectrum observed for the aluminium(III) complex is more likely to be associated with a quartet-state complex as discussed later on.

In order to obtain the spin-density distribution in the tmtd semidione, we examined its liquid solution e.s.r. spectrum after reduction by Li in ethereal solvent. The spectrum consists of a quartet due to the hyperfine coupling of the unpaired electron with the ^7Li nucleus, $I = \frac{3}{2}$. At the wings of the spectrum much weaker e.s.r. lines due to radicals containing a naturally occurring ^{13}C nucleus coupled to the unpaired electron were detected. Two ^{13}C hyperfine coupling constants were determined with $a_{^{13}C} =$ 4.8 and 1.6 G.

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† 1,1,4,4-Tetramethyl-1,2,3,4-tetrahydronaphthalene-2,3-dionate(1−).

DISCUSSION

Spin-density Distribution and Conformation of the Uniradical.—As reported above, two ^{13}C hyperfine coupling constants of 4.8 and 1.6 G were detected. The latter value was attributed to that of a carbonyl group, by comparison with other aliphatic semidiones.[6]

By using the semi-empirical relation (1) one obtains

$$a_{CO}^{C} = (S_C + Q_{CC}^{C} + Q_{CO}^{C})\rho_C + Q_{OC}^{C}(0.5 - \rho_C) \quad (1)$$

$\rho_C = 0.29$, in agreement with the ρ_C values usually found for aliphatic semidiones, which are in the range 0.28—0.30.[6]

The largest ^{13}C hyperfine coupling constant corresponds to the methyl position and possibly also to the ^{13}C in the α position with respect to the carbonyl carbon atom. The ^{13}C atoms in the methyl groups are in the β position with respect to the carbons bearing spin density.

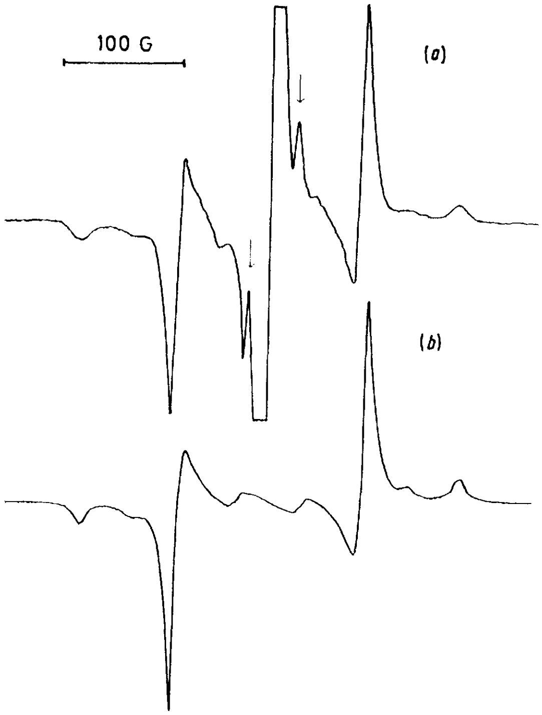

FIGURE 1 Experimental (*a*) and calculated (*b*) e.s.r. spectra of the [Sr(tmtd)$_2$] complexes in frozen 2-methyltetrahydrofuran. The arrows show the e.s.r. lines due to conformation II, not included in the simulation

The semi-empirical relation (2) giving the hyperfine coupling constant of the β carbons is well known where

$$a_{\beta}^{C} = B\rho_C\cos^2\theta \quad (2)$$

B is a parameter depending on the nature of the compound, ρ_C is the π spin density on the trigonal carbon atom, and θ is the dihedral angle between the axis of the $2p_\pi$ atomic orbital of the C atom and the Cα–Cβ bond. The hyperfine coupling constant of the β carbon atom was measured by Russell *et al.*[6] for the 3,3,5,5-tetramethylcyclopentane-1,2-semidione which is certainly planar and hence has θ = 30°. From their value of 5.9 G, one obtains $B\rho_C = 7.9$ G.

In the tmtd case, the dihedral angle obtained by relation (2) with $B\rho_C = 7.9$ G is 39°, which does not correspond to any usual conformation for six-membered rings. We believe instead that the tmtd radical interconverts rapidly between two equivalent half-chair conformations in which θ for each methyl carbon would correspond alternately to 0° and 60°, with hyperfine coupling constants of 7.9 and 2 G respectively. The mean value of 4.9 G is in excellent agreement with the experimental value.

TABLE 1

Experimental zero-field splitting parameters and conformational parameters of the [M(tmtd)$_2$] complexes

M	D/G	E/G	Conformation [a,b]	R_{OM} [a,c]/Å	θ [a,d]/°	$R_O + R_M$ [e]/Å
Be	91	13	IV	1.91	60	1.71
	67	[f]	II	2.15	90	
Mg	81	1	V	2.13	0	2.05
	216	7	I	2.11	0	
	232	7	I	2.06	0	
Zn	65	[f]	II	2.20	90	2.09
	46	[f]	II	2.67	90	
Ca	130	$E \neq 0$ [f]	I	2.54	0	2.34
	136	$E \neq 0$ [f]	I	2.50	0	
	170	0	III	2.33	90	
Sr	41	[f]	II	2.83	90	2.50
	154	0	III	2.47	90	

[a] Obtained by comparison of experimental and calculated zero-field splitting parameters (see text). [b] See Figure 2. [c] Distance between the cation and the nearest oxygen. [d] Angle between the planes of the two π distributions. See Figure 2. [e] Sum of the van der Waals radii of the oxygen atom and the cation. [f] Not determined.

Further support to the interconversion between the two conformations might be obtained by following the ^{13}C hyperfine coupling constant dependence on temperature, but this was prevented by a severe decrease in the intensity of the e.s.r. lines on decreasing the temperature.

Conformations of the Biradical Complexes.—In order to explain the different zero-field splitting for the different types of complexes listed in Table 1, we calculated the D and E values for different geometries of the complex. The method of calculation is described elsewhere.[7] It involves the calculation of the dipolar interaction between point dipoles placed at the points of maximum density (±0.83 Å along the z axis of the $2p_z$ atomic orbitals that form the π molecular orbital).

We started by assuming that the oxygen–metal bond had a length fairly close to the sum of the van der Waals radii of the two atoms, as observed for similar complexes.[2]

Of several conformations checked for each complex, only one allowed us to fit both the experimental D and E values. The selected conformations are shown in Figure 2. In conformations II and V, the semidione behaves like a unidentate ligand, while in conformations I and III it behaves as a bidentate ligand. These latter conformations are usually found in biradical complexes of non-transition bivalent metals.[1,2] In the barium and strontium cases the two conformations III and I, corresponding to perpendicular and planar conformations of the two π distributions in the two radicals, have similar concentrations, as already found for the analogous complexes of the isoelectronic di-imine radical anions.[2] In the case of the magnesium and calcium complexes, two planar complexes are formed having slightly different distances between the two radical anions. We attribute this different distance to a different interaction between the methyl groups of the radicals in these two complexes. In fact, the biradical complex belongs to the C_{2v} or C_{2h} symmetry point group since the two radicals in the half-chair conformation have methyl groups eclipsed and staggered, respectively. The interaction between the non-bonded atoms in the two cases can be sufficiently strong to account for the slightly different distances between the two ligands.

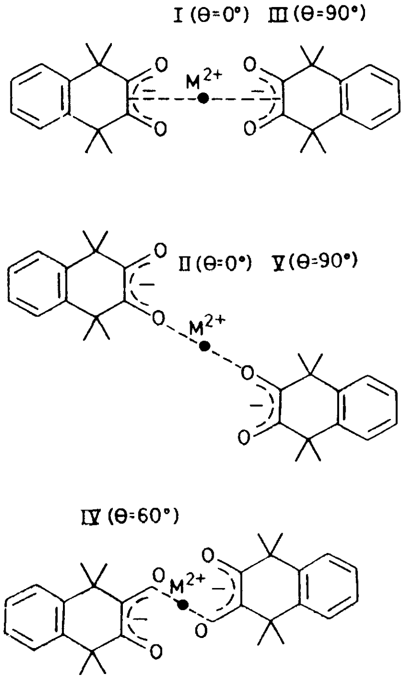

FIGURE 2 Conformations of the complexes giving the best fit between the experimental and calculated D and E values. Θ is the angle of rotation of a tmtd⁻ radical with respect to the other one around the dashed line

In the planar complexes of the largest ions Sr^{2+} and Ba^{2+}, the inter-radical distances are independent of the conformations of the two radicals, and the e.s.r. spectra of the two species, if both are present, coincide.

One interesting feature observed is the difference in the zero-field splitting parameters between the planar and the perpendicular conformations of the same metal complex, this difference being small for complexes of the lighter cations and increasing with the atomic weight of the metal. A similar feature was observed in the di-imine radical anion complexes and it was attributed to a spin-orbit contribution to the zero-field splitting parameters.[2] Our present results confirm this interpretation. In fact, the calculation of D and E based on the pure dipolar contribution in the planar conformation did not reproduce the experimental values, using as the oxygen-metal distance the sum of the van der Waals radii. However, the addition of a spin-orbit contribution could explain this discrepancy, as will be discussed later on.

The conformation of the beryllium complex is different with respect to all the others (conformation IV in Figure 2). This may be due to a compromise between the tendency of Be orbitals to reach maximum overlap with lone-pair oxygen orbitals and the steric hindrance of the two radicals due to the small ionic radius of the Be^{2+} cation.

Structure and Conformation of the Aluminium Complex.—If we attribute the e.s.r. spectrum of the frozen solution to a triplet species $[Al(tmtd)_2]^+$ its apparent D value should be 356 G. This value is too high to be explained by any biradical conformation. A triradical aggregate $[Al(tmtd)_3]$ in a quartet state might, however, be responsible for the observed spectrum. In fact, a quartet-state system in a frozen solution exhibits an e.s.r. spectrum very similar to that of a triplet state, apart from an absorption line at the centre of the spectrum.[8] In our case, the central quartet line might be present but obscured by the very intense e.s.r. line due to a doublet species that we detected in the e.s.r. spectra of all the complexes. In a quartet-state spectrum of a frozen solution the parameter D is equal to a quarter of the field separation of the outermost absorption peaks, whereas in a triplet-state spectrum D is given by one half of the same field separation. This implies that in the $[Al(tmtd)_3]$ complex the zero-field parameter D is 178 G, a value that compares well with those of other complexes formed by tmtd.

Spin-Orbit Contribution to the Zero-field Splitting Parameters.—Triplet states can be mixed by spin-orbit interaction with nearby singlet states. This mixing gives rise to a term in the spin Hamiltonian that has the same form as the spin-spin dipolar interaction.[9]

In the following discussion, we will consider only the strontium(II) complexes, which show the maximum deviation between calculated and experimental zero-field splitting. Moreover, we will consider the mixing between the semidione orbitals and the strontium $5p$ orbitals only, since the spin-orbit contribution to the zero-field splitting parameters due to the mixing with the $4d$ orbitals can be neglected, as discussed later on.

In the $R^-{-}Sr^{2+}{-}R^-$ planar complex, the triplet state can be described by the wave function ${}^3\psi = |\phi_\sigma\bar{\phi}_\sigma\phi_\pi\phi_\pi'|$, where $\phi_\sigma = N(c_Z{}^M p_Z{}^M + n_1{}^O + n_2{}^O - n_3{}^O - n_4{}^O)$, $\phi_\pi = N'(c_Y{}^M p_Y{}^M + \pi_A + \pi_B)$, $\phi_\pi' = 2^{-\frac{1}{2}}(\pi_A - \pi_B)$; $n_i{}^O$ represent the oxygen lone-pair orbitals, π_A and π_B are the ligand π molecular orbitals of the two unpaired electrons, and $p_y{}^M$ and $p_z{}^M$ are the $5p$ strontium orbitals that are allowed to be mixed with, respectively, π_A and π_B orbitals and with the oxygen's lone pairs through coefficients $c_y{}^M$ and $c_z{}^M$ (Figure 3).

The closest in energy singlet-state wave function that can be mixed with ${}^3\psi$ is found to be that given in (3).

$$ {}^1\psi = 2^{-\frac{1}{2}}(|\phi_\sigma\phi_\pi\bar{\phi}_\pi\bar{\phi}_\pi'| - |\bar{\phi}_\sigma\phi_\pi\bar{\phi}_\pi\phi_\pi'|) \qquad (3) $$

Since the spin–orbit coupling constant of strontium in the $5p^2$ configuration is far larger than that of the other atoms in the complex [10] the spin–orbit coupling Hamiltonian can be expressed simply as (4). Straightforward

$$\mathscr{H}_{SO} = \lambda_{Sr} \bar{L} \cdot \bar{S} \qquad (4)$$

application of second-order perturbation theory on the basis of $^3\psi$ and $^1\psi$ with the perturbing Hamiltonian (5) leads to the spin Hamiltonian (6) [11] and the experimental

$$\mathscr{H}' = \mathscr{H}_{SO} + (g_e\bar{S} + \bar{L}) \cdot B \qquad (5)$$

$$\mathscr{H}_S = \beta\bar{B} \cdot \tilde{g} \cdot \bar{S} + D_{SO}S_z^2 + E_{SO}(S_x^2 - S_y^2) \qquad (6)$$

zero-field splitting parameters for the strontium planar complexes are given by $D_{exp.} = D_{SS} + D_{SO}$ and $E_{exp.} = E_{SS} + E_{SO}$. The spin–orbit contributions D_{SO} and E_{SO} are given by (7) and (8) [11] where $\Lambda_{kk} = \langle{}^3\psi|L_k|{}^1\psi\rangle \langle{}^1\psi|L_k|{}^3\psi\rangle$ ($k = x$, y, or z) and $\Delta E = E_{1\psi} - E_{3\psi}$.

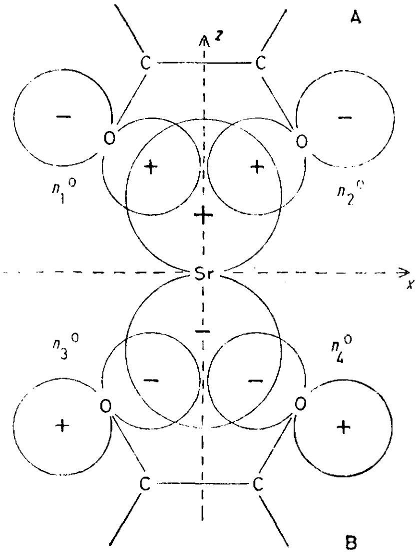

FIGURE 3 The [Sr(tmtd)$_2$] planar complex

$$D_{SO} = -\frac{\lambda_{Sr}^2}{\Delta E}\left[\Lambda_{zz} - \tfrac{1}{2}(\Lambda_{xx} + \Lambda_{yy})\right] \qquad (7)$$

$$E_{SO} = \frac{\lambda_{Sr}^2}{2\Delta E}(\Lambda_{yy} - \Lambda_{xx}) \qquad (8)$$

We found that $\Lambda_{yy} = \Lambda_{zz} = 0$ by symmetry, and equations (7) and (8) reduce to (9).

$$D_{SO} = -E_{SO} = -\frac{\lambda_{Sr}^2}{2\Delta E}\Lambda_{xx} \qquad (9)$$

Evaluation of the D_{SO} and E_{SO} contributions to the zero-field splitting parameters through equation (9) was not carried out because of the lack of a reliable estimate of the quantity Λ_{xx} which depends on the amount of mixing of the strontium $5p$ orbitals with tmtd orbitals. Nevertheless, we expect that according to equation (9) D_{SO} and E_{SO} have the same absolute value but opposite signs.

On the assumption that the oxygen–metal distance in the strontium complex, as for the other complexes, is equal to the sum of the van der Waals radii of the two atoms, then D_{SS} and E_{SS} contributions can be calculated. For the planar strontium complex $D_{SS} = -134$ and $E_{SS} = 2$ G (see Table 2). From the differences ($D_{exp.} - D_{SS}$) and ($E_{exp.} - E_{SS}$) one obtains $D_{SO} = 22$ G and $E_{SO} = -22$ G.

As expected, on the basis of the above treatment, the D_{SO} and E_{SO} values obtained have the same absolute value but different signs.

It is worth noting that D_{SO} and E_{SO} values depend on the spin–orbit coupling, λ_{Me}, and on the Λ_{xx} value. On increasing the metal size, the former term increases whereas the latter decreases, since it depends on the strength of the ligand–metal bond. In the Sr^{2+} case the two factors give the maximum value of D_{SO} and E_{SO} in the series of the five alkaline-earth metals, as observed in the present complex and in other similar complexes.[2,7]

The mixing of the semidione orbitals with the $4d$ strontium orbitals does not affect the D_{SO} and E_{SO} values. In fact, the spin–orbit coupling constant is smaller in the $4d^2$ configuration (70 cm^{-1}) than in the $5p^2$ (207 cm^{-1}). Since D_{SO} and E_{SO} depend on λ_{Sr}^2, by assuming the same admixture coefficients for the two kinds of orbitals, the contribution to zero-field splitting parameters due to the $4d$ orbitals admixture should be one order of magnitude smaller than that due to the $5p$ orbitals.

TABLE 2

Experimental and calculated zero-field splitting parameters (G) for Sr^{2+} and Ba^{2+} planar complexes

	$\lvert D_{exp.}\rvert$ [a]	$\lvert E_{exp.}\rvert$ [a]	$D_{calc.}$ [b]	$E_{calc.}$ [b]
Sr	112	20	−134	2
Ba	115	6	−112	2

[a] In the calculations of the spin–orbit contributions it is assumed $D_{exp.} < 0$ and $E_{exp.} < 0$ (see text). [b] Calculated for an oxygen–cation distance equal to the van der Waals radii sum. The calculation takes into account the spin–spin dipolar interaction only. See text.

In the Ba^{2+} case, the metal orbitals involved in mixing with the semidione orbitals might be the $5d$ and $6p$. The spin-orbit coupling constants in the configurations $5d^2$ and $6p^2$ are similar [10] and the contributions to D_{SO} and E_{SO} due to both kinds of orbitals should be taken into account. We extended the analysis performed above for the p orbitals to the case of the d orbitals. We found here that all three components Λ_{ii} ($i = x,y,z$) [see equations (7)—(9)] are different from zero which implies that the symmetry relation $D_{SO} = -E_{SO}$ no longer holds. The results collected in Table 2 show that this is indeed the case and suggest that the $5d$ orbitals are involved in the Ba^{2+}–tmtd bond.

Finally, we note that the spin–orbit contribution to the zero-field splitting parameters in the perpendicular complexes of type III is prevented by symmetry.

Conclusions.—We have shown that the conformations of the complexes involving paramagnetic ligands with a known spin-density distribution can be determined in detail by reproducing the experimental zero-field splitting parameters in a point–dipole approximation.

Moreover, we have shown that singlet–triplet mixing due to the spin–orbit coupling is in some cases responsible for large deviations between calculated and experimental zero-field splitting parameters, as in a number of complexes of strontium with oxygen-containing ligands.

When such a spin–orbit contribution to the zero-field splitting parameters is present, information on the nature of the metal–ligand bonds can be inferred.

This work was supported by the Consiglio Nazionale delle Ricerche (C.N.R.) through its Centro di Studio sugli Stati Molecolari Radicalici ed Eccitati.

[0/619 *Received*, 28*th April*, 1980]

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