Electron Spin Resonance Spectra of some Low-spin Ruthenium(III) Complexes: A Probe for Solvation Effects

By J. Barrie Raynor * and Bojana G. Jeliazkowa, Department of Chemistry, University of Leicester, Leicester LE1 7RH

Electron spin resonance spectra of a series of low-spin d^5 complexes of the type $[RuL_4X_2]^+$ [L_4 = (ethylenediamine)$_2$, 1,4,8,11-tetra-azacyclotetradecane, or 1,9-diamino-3,7-diazanonane; X = Cl, Br, I, or NCS] in water, dimethyl sulphoxide, dimethylformamide, and hexamethylphosphoramide have been recorded. From analysis of the three well resolved g features a thorough understanding of the bonding in the complexes and of their products of solvolysis is obtained.

THE solvolysis of ruthenium(III) amine complexes is slow and much is understood about the kinetics and mechanisms of many systems.[1] The effects of stereochemistry and chelation upon solvolysis in both aqueous and mixed water–organic solvent mixtures is less well established. One way to observe the subtle changes to the ligand field that take place as successive steps of solvolysis occur, *viz.* $[RuL_4X_2]^+ \longrightarrow [RuL_4X(solv)]^{2+} \longrightarrow [RuL_4(solv)_2]^{3+}$ (solv = solvent), is to study the e.s.r. spectrum of each species, which are readily observed in the frozen solution. From analysis of the e.s.r. g tensors, the ligand-field parameters may be calculated and correlated with the nature of the species in solution.

We have studied the solvolysis of the following complexes in water, dimethylformamide (dmf), dimethyl sulphoxide (dmso), and hexamethylphosphoramide (hmpa): *cis*-$[Ru(en)_2Br_2]ClO_4$, *trans*-$[Ru(en)_2Cl_2]ClO_4$, *trans*-$[Ru(en)_2Br_2]ClO_4$, *trans*-$[Ru(en)_2I_2]I$, *trans*-$[Ru(en)_2(NCS)_2]NCS$, *trans*-$[Ru(cyclam)Cl_2]ClO_4$, and *trans*-$[Ru(dadn)X_2]ClO_4$ (X = Cl or Br) where en = ethylenediamine, cyclam = 1,4,8,11-tetra-azacyclotetradecane, and dadn = 1,9-diamino-3,7-diazanonane.

E.s.r. measurements have been carried out on other ruthenium(III) complexes by de Simone,[2] Hill,[3] Hudson and Kennedy,[4] Sakaki *et al.*,[5] Medhi and Agarwala,[6] and Manoharan *et al.*[7] The only one in which there is significant chemical resemblance is the study of $[Ru(NH_3)_5X]Cl_2$ (X = Cl, Br, or I).[5]

EXPERIMENTAL

All the complexes were prepared by the published procedures and supplied by Professor C. K. Poon.[8] E.s.r. spectra of frozen solutions were recorded on a Varian E3 spectrometer at 77 K. In order to prevent hydrolysis of the parent dihalide complexes for the measurement of their e.s.r. spectra, an excess of the appropriate lithium halide was added. In other cases, an excess of silver perchlorate was added to remove all halide and allow full solvation. It was found that on adding a small amount of silver perchlorate a distinct and reproducible intermediate solvated species could be obtained in which one co-ordinating halide was replaced by a solvent molecule. In the case of solvolysis by water, some ethanol was added immediately before freezing in order to make a good glass at 77 K for the e.s.r. measurements. It is known that up to 40% ethanol does not affect the hydrolysis.[9]

RESULTS AND DISCUSSION

The e.s.r. spectra of frozen solutions at 77 K all showed well resolved spectra exhibiting three g features ranging from 0.97 to 3.44, with an error of ± 0.01 (see Table). In some cases where incomplete or partial hydrolysis had taken place, the spectra consisted of the sum of two species. It was this sort of measurement that often allowed detection of the intermediate monosolvate, see Figure 1. The rate of solvolysis of ruthenium(III) complexes is known to be slow. No hyperfine coupling to Ru or halogens was detected.

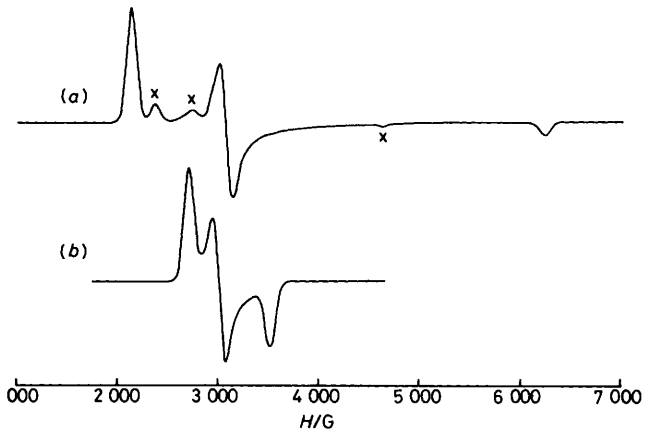

FIGURE 1 E.s.r. spectra of *trans*-$[Ru(dadn)Br_2]ClO_4$ at 77 K: (*a*) showing the spectrum X of some partial hydrolysis product; (*b*) after complete hydrolysis (1 G = 10^{-4} T)

Theory of the $^2T_2(t_2^5)$ *Ground State.*—The theory of low-spin d^5 metal ions with octahedral symmetry was developed by Griffith,[10,11] Thornley,[12] and others [3,13] and extended to systems of lower than cubic symmetry by Hill [3] who presented expressions which included admixture of excited $t_2^4e^1$ states into the ground state (configuration interaction). In this paper, sufficient theory will only be given to make clear the origin of the parameters deduced, and, where possible, their physical significance.

The equations of Griffith,[10] (1)—(3), which were deduced from the matrix elements of the spin Hamiltonian of the lowest Kramer's doublet involving the t_2 set of orbitals, were used where A, B, and C are the coefficients

E.s.r. spectral data

Complex	Solvent	g_x	g_y	g_z	A	B	C	k	$6\epsilon/\xi$	E/ξ	Δ/ξ	$\lvert 6\epsilon/\Delta \rvert$
(1) *cis*-$[Ru(en)_2Br_2]ClO_4$	dmf	−2.41	1.02	2.82	0.875	0.463	0.140	1.123	0.450	−1.052	−0.428	1.053
	dmso	−2.41	1.02	2.79	0.874	0.466	0.140	1.114	0.453	−1.051	−0.414	1.094
	H_2O	−2.41	1.02	2.76	0.872	0.468	0.140	1.104	0.456	−1.050	−0.401	1.137
	hmpa	−2.48	1.02	2.76	0.869	0.472	0.147	1.124	0.481	−1.050	−0.378	1.271
Monosubstituted (1)	dmf	−2.43	1.40	2.78	0.864	0.493	0.101	1.187	0.332	−1.028	−0.319	1.040
	dmso	−2.44	1.53	2.71	0.857	0.507	0.088	1.196	0.296	−1.021	−0.262	1.131
	H_2O	−2.44	1.61	2.72	0.856	0.511	0.080	1.215	0.269	−1.018	−0.250	1.075
	hmpa	−2.45	1.78	2.73	0.852	0.520	0.064	1.256	0.216	−1.013	−0.218	0.989
Disubstituted (1)	dmf	−2.32	1.80	2.50	0.843	0.536	0.051	1.164	0.175	−1.007	−0.158	1.165
	dmso	−2.08	1.72	2.54	0.856	0.516	0.036	1.096	0.210	−1.010	−0.246	0.487
	H_2O	−2.32	1.80	2.51	0.843	0.535	0.051	1.166	0.174	−1.007	−0.162	1.077
	hmpa	−2.27	1.81	2.51	0.845	0.533	0.045	1.156	0.154	−1.007	−0.171	0.900
(2) *trans*-$[Ru(cyclam)Cl_2]ClO_4$	dmf	−1.95	1.16	3.18	0.907	0.414	0.080	1.142	0.234	−1.072	−0.717	0.326
	dmso	−1.97	1.16	3.20	0.907	0.413	0.081	1.154	0.239	−1.073	−0.719	0.333
	H_2O	−1.87	1.08	3.44	0.922	0.380	0.079	1.197	0.224	−1.106	−0.913	0.246
	hmpa	−1.90	1.09	3.35	0.917	0.391	0.082	1.175	0.233	−1.094	−0.849	0.275
Monosubstituted (2)	dmf	−2.28	1.85	2.40	0.837	0.546	0.042	1.138	0.147	−1.005	−0.120	1.225
	dmso	−2.44	1.77	2.51	0.846	0.530	0.064	1.218	0.221	−1.010	−0.178	1.244
	H_2O	−2.37	1.85	2.48	0.839	0.542	0.050	1.183	0.175	−1.006	−0.130	1.346
	hmpa	−2.25	1.84	2.44	0.841	0.540	0.040	1.139	0.139	−1.005	−0.144	0.970
Disubstituted (2)	dmf	−2.20	1.95	2.25	0.828	0.561	0.025	1.102	0.088	−1.001	−0.063	1.400
	dmso	−2.07	1.88	2.32	0.839	0.544	0.019	1.071	0.066	−1.003	−0.130	0.510
	H_2O	−2.25	1.89	2.34	0.833	0.552	0.035	1.124	0.125	−1.003	−0.097	1.287
	hmpa	−2.21	1.91	2.32	0.833	0.553	0.030	1.113	0.104	−1.003	−0.094	1.107
(3) *trans*-$[Ru(en)_2Cl_2]ClO_4$	dmf	−2.26	1.10	3.05	0.891	0.440	0.116	1.168	0.356	−1.059	−0.561	0.635
(4) *trans*-$[Ru(en)_2Br_2]ClO_4$	dmf	−2.36	0.99	3.02	0.888	0.440	0.137	1.166	0.427	−1.064	−0.543	0.786
(5) *trans*-$[Ru(en)_2I_2]I$	dmf	−2.31	0.97	3.04	0.891	0.434	0.134	1.156	0.415	−1.068	−0.576	0.721
(6) *trans*-$[Ru(en)_2(NCS)_2]NCS$	dmf	−2.22	1.03	3.04	0.893	0.433	0.120	1.142	0.366	−1.064	−0.591	0.620
(3)	dmso	−2.26	1.11	3.05	0.891	0.440	0.115	1.170	0.353	−1.058	−0.558	0.632
(4)	dmso	−2.36	1.04	3.01	0.886	0.444	0.132	1.172	0.411	−1.060	−0.525	0.783
(5)	dmso	−2.37	0.97	3.01	0.887	0.440	0.140	1.163	0.438	−1.065	−0.541	0.809
(6)	dmso	−2.25	1.01	3.02	0.892	0.435	0.125	1.140	0.384	−1.064	−0.577	0.665
(3)	H_2O	−2.25	1.10	3.02	0.890	0.442	0.115	1.156	0.355	−1.057	−0.551	0.644
(4)	H_2O	−2.22	1.04	3.07	0.894	0.431	0.118	1.154	0.361	−1.065	−0.602	0.600
(5)	H_2O	−2.26	1.02	3.10	0.895	0.429	0.124	1.170	0.379	−1.068	−0.608	0.623
(6)	H_2O	−2.25	1.11	3.07	0.892	0.438	0.114	1.174	0.349	−1.060	−0.571	0.611
(3)	hmpa	−2.25	1.19	3.04	0.889	0.446	0.105	1.179	0.325	−1.052	−0.535	0.608
(4)	hmpa	−2.31	1.08	3.04	0.889	0.442	0.122	1.175	0.380	−1.059	−0.545	0.697
(5)	hmpa	−2.34	1.04	3.04	0.888	0.441	0.130	1.176	0.402	−1.062	−0.546	0.738
(6)	hmpa	−2.20	1.05	3.01	0.892	0.436	0.116	1.131	0.355	−1.061	−0.578	0.614
Monosubstituted (3)	dmf	−2.42	1.75	2.76	0.855	0.514	0.064	1.250	0.214	−1.014	−0.242	0.885
(4)	dmf	−2.49	1.63	2.75	0.855	0.512	0.082	1.241	0.277	−1.018	−0.245	1.131
(5)	dmf	−2.51	1.60	2.73	0.854	0.513	0.087	1.234	0.295	−1.019	−0.238	1.238
(6)	dmf	−2.28	1.78	2.71	0.857	0.514	0.048	1.207	0.161	−1.012	−0.250	0.643
(3)	dmso	−2.40	1.50	2.72	0.860	0.503	0.088	1.182	0.292	−1.022	−0.282	1.035
(4)	dmso	−2.44	1.43	2.59	0.859	0.503	0.099	1.170	0.381	−1.025	−0.274	1.208
(5)	dmso	−2.38	1.35	2.67	0.862	0.497	0.102	1.132	0.339	−1.027	−0.298	1.135
(6)	dmso	−2.44	1.42	2.67	0.858	0.504	0.100	1.162	0.335	−1.024	−0.268	1.253
(3)	H_2O	−2.38	1.73	2.58	0.847	0.527	0.063	1.186	0.215	−1.011	−0.188	1.148
(4)	H_2O	−2.41	1.72	2.71	0.854	0.517	0.066	1.227	0.223	−1.014	−0.232	0.963
(5)	H_2O	−2.41	1.74	2.51	0.842	0.536	0.065	1.177	0.225	−1.010	−0.153	1.477
(6)	H_2O	−2.25	1.80	2.44	0.842	0.538	0.044	1.130	0.153	−1.006	−0.151	1,011
(3)	hmpa	−2.39	1.71	2.63	0.850	0.522	0.066	1.198	0.223	−1.012	−0.208	1.073
(4)	hmpa	−2.41	1.74	2.65	0.850	0.523	0.064	1.215	0.219	−1.012	−0.205	1.068
(5)	hmpa	−2.41	1.74	2.73	0.854	0.516	0.064	1.237	0.216	−1.014	−0.235	0.917
(6)	hmpa	−2.51	1.78	2.76	0.851	0.520	0.069	1.280	0.234	−1.013	−0.215	1.087
Disubstituted (3)	dmf	−2.39	1.74	2.67	0.852	0.520	0.063	1.215	0.212	−1.012	−0.217	0.973
(5)	dmf	−2.44	1.77	2.63	0.847	0.528	0.064	1.224	0.220	−1.011	−0.185	1.189
(6)	dmf	−2.25	1.81	2.67	0.855	0.517	0.043	1.195	0.143	−1.010	−0.236	0.604
(3)	dmso	−2.42	1.72	2.52	0.843	0.534	0.068	1.178	0.235	−1.010	−0.158	1.492
(5)	dmso	−2.41	1.72	2.48	0.841	0.537	0.067	1.164	0.234	−1.010	−0.145	1.613
(3)	H_2O	−2.21	1.82	2.39	0.840	0.542	0.039	1.111	0.134	−1.005	−0.137	0.974
(4)	H_2O	−2.29	1.80	2.42	0.839	0.542	0.048	1.135	0.167	−1.006	−0.135	1.242
(5)	H_2O	−2.30	1.80	2.42	0.839	0.542	0.049	1.137	0.171	−1.006	−0.133	1.288
(6)	H_2O	−2.23	1.83	2.44	0.842	0.538	0.039	1.131	0.136	−1.005	−0.150	0.906
(3)	hmpa	−2.29	1.82	2.48	0.842	0.537	0.046	1.155	0.158	−1.006	−0.154	1.032
(5)	hmpa	−2.27	1.81	2.48	0.843	0.536	0.045	1.148	0.155	−1.007	−0.160	0.970
(6)	hmpa	−2.24	1.82	2.48	0.844	0.535	0.041	1.142	0.142	−1.006	−0.165	0.859
(7) *trans*-$[Ru(dadn)Cl_2]ClO_4$	dmf	−2.11	0.98	3.14	0.903	0.414	0.114	1.137	0.341	−1.078	−0.697	0.488
(8) *trans*-$[Ru(dadn)Br_2]ClO_4$	dmf	−2.13	1.04	3.11	0.900	0.422	0.110	1.143	0.330	−1.070	−0.655	0.504
(7)	dmso	−2.12	0.98	3.14	0.903	0.415	0.115	1.140	0.344	−1.078	−0.693	0.496
(8)	dmso	−2.15	1.06	3.10	0.898	0.426	0.110	1.148	0.331	−1.067	−0.836	0.520
(7)	H_2O	−2.12	0.98	3.14	0.903	0.415	0.115	1.140	0.344	−1.078	−0.693	0.496
(8)	H_2O	−2.13	1.03	3.11	0.900	0.422	0.111	1.141	0.333	−1.017	−0.658	0.506
(7)	hmpa	−2.11	1.04	3.16	0.903	0.417	0.108	1.154	0.321	−1.074	−0.687	0.467
(8)	hmpa	−2.14	1.06	3.14	0.900	0.422	0.108	1.159	0.325	−1.070	−0.659	0.494
Monosubstituted (7)	dmf	−2.13	1.89	2.37	0.839	0.543	0.024	1.101	0.083	−1.003	−0.134	0.618

TABLE (*continued*)

Complex		Solvent	g_x	g_y	g_z	A	B	C	k	$6\epsilon/\xi$	E/ξ	Δ/ξ	$\lvert 6\epsilon/\Delta \rvert$
Monosubstituted	(8)	dmf	−2.10	1.91	2.37	0.840	0.543	0.019	1.098	0.065	−1.003	−0.136	0.480
	(7)	dmso	−2.34	1.47	2.76	0.865	0.494	0.085	1.172	0.280	−1.024	−0.320	0.873
	(8)	dmso	−2.38	1.43	2.80	0.867	0.490	0.093	1.186	0.304	−1.028	−0.334	0.909
	(7)	H_2O	−2.38	1.74	2.57	0.846	0.529	0.062	1.185	0.212	−1.010	−0.182	1.168
	(8)	H_2O	−2.34	1.75	2.57	0.848	0.528	0.057	1.177	0.196	−1.010	−0.189	1.033
	(7)	hmpa	−2.28	1.74	2.46	0.844	0.534	0.053	1.129	0.183	−1.008	−0.163	1.120
	(8)	hmpa	−2.27	1.78	2.45	0.842	0.537	0.048	1.133	0.166	−1.007	−0.154	1.078
Disubstituted	(7)	dmf	−2.20	1.84	2.30	0.834	0.550	0.036	1.089	0.126	−1.003	−0.102	1.236
	(8)	dmf	−2.20	1.83	2.28	0.833	0.552	0.037	1.081	0.130	−1.003	−0.096	1.351
	(7)	dmso	−2.18	1.87	2.46	0.843	0.536	0.030	1.133	0.105	−1.005	−0.161	0.652
	(8)	dmso	−2.20	1.88	2.45	0.842	0.539	0.031	1.138	0.108	−1.005	−0.151	0.719
	(7)	H_2O	−2.26	1.78	2.39	0.839	0.542	0.047	1.114	0.165	−1.006	−0.134	1.232
	(8)	H_2O	−2.23	1.82	2.39	0.839	0.543	0.040	1.116	0.141	−1.005	−0.133	1.058
	(7)	hmpa	−2.28	1.80	2.39	0.838	0.544	0.047	1.124	0.165	−1.006	−0.126	1.312
	(8)	hmpa	−2.24	1.80	2.39	0.839	0.542	0.043	1.114	0.151	−1.005	−0.135	1.123

$$g_x = 2[-2AC + B^2 + \sqrt{2}kB(A - C)] \quad (1)$$

$$g_y = 2[-2AC - B^2 - \sqrt{2}kB(A + C)] \quad (2)$$

$$g_z = 2[A^2 - B^2 + C^2 + k(A^2 - C^2)] \quad (3)$$

of the orbitals comprising the Kramer's doublets and are themselves related by equation (4).

$$A^2 + B^2 + C^2 = 1 \quad (4)$$

The e.s.r. experiments do not yield the sign of g and so all combinations of signs of g_x, g_y, and g_z need to be considered in solving the equations. Furthermore, the labelling x, y, and z is arbitrary and so 48 possible combinations need to be considered. The orbital-reduction factor, k, represents the averaged orbital-reduction factor of the pure t_2^5 ground state and the excited $t_2^4(^1T_{2g})e^1$ and $t_2^4(^3T_2)e^1$ states and is expected to be <1.0. This is not necessarily so, however, since many factors enter into its value, in particular the low-lying excited states which cause a substantial increase in the effective orbital angular momentum of the ground state.[10] It follows that one cannot equate k with delocalisation or covalency and little can be concluded from it.

The values of the coefficients A, B, and C may be used to calculate the orbital energies and the crystal-field parameters as functions of ξ, the one-electron spin–orbit coupling constant which must be positive. The orbital energies are defined in Figure 2. Because the symmetry

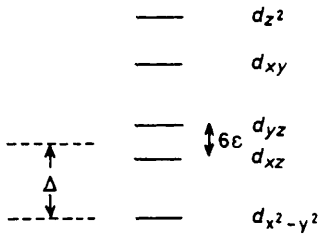

FIGURE 2 The order of the energy levels and definition of Δ and 6ϵ

of the *trans* complexes is at best C_{2v} (ignoring the non-planarity of the carbon atoms relative to the nitrogens), the z axis is defined as going through the *trans* ligands, and the x and y axes passing between the equatorial nitrogen atoms, as in Figure 3. This causes the d_{xy} and $d_{x^2-y^2}$ orbitals to be defined in a less traditional way, *i.e.* the d_{xy} orbital will line up with the four equatorial nitrogen atoms. The notation of Griffith for t_2 and e orbitals is used, remembering that t_2 encompasses the $d_{x^2-y^2}$, d_{xz}, d_{yz} group of orbitals and e encompasses the d_{xy}, d_{z^2} pair. The parameter Δ is the splitting of the t_2 orbitals by the axial component of the crystal field and

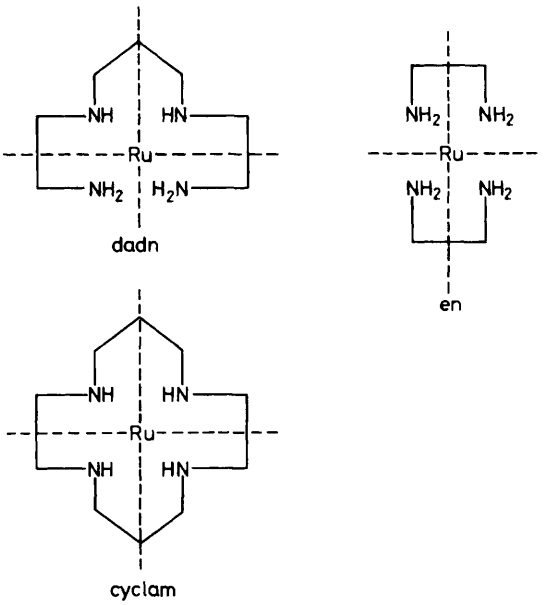

FIGURE 3 The x and y axes (dashed lines) for the complexes studied

is defined as negative for a d^5 ion if the $d_{x^2-y^2}$ orbital lies lower than the $d_{xz,yz}$ degenerate pair. The rhombic splitting of $d_{xz,yz}$ in the absence of spin–orbit interactions is defined as 6ϵ. This parameter may be positive or negative depending on the definition of the x and y axes so its sign is really of no consequence. E is the average excitation energy for the $t_2^4e^1$ configuration. These parameters are related by equations (5)—(7).

$$\epsilon/\xi = -\left(\frac{A\sqrt{2} + B}{3\sqrt{2}}\right)\left(\frac{C}{C^2 - A^2}\right) \quad (5)$$

$$\Delta/\xi = -A/B\sqrt{2} - 1/2 + (3A/C)(\epsilon/\xi) \quad (6)$$

$$E/\xi = -A/B\sqrt{2} - (2/3)(\Delta/\xi) \quad (7)$$

More detailed equations which consider orbital-reduction factors for each of the excited states, and their respective energies, have been presented by Hill,[3] but their solution is not possible without knowledge of a properly assigned optical spectrum. This is not possible with our complexes. The seven equations have seven unknowns A, B, C, k, Δ/ξ, ϵ/ξ, and E/ξ and may readily be solved using standard computer routines.[14] Many possible solutions are obtained from the 48 possible combinations of experimental g values. Selection is helped if g_z is defined as having the largest g value since in the strong axial field limit $g_{\parallel} = 4$ and $g_{\perp} = 0$. Solutions were rejected where k lay outside the limits 0.9—1.3, ϵ/ξ outside −0.1 to 0.1, E/ξ outside −0.5 to −2, and $|\Delta| > |E|$. A self-consistent set of solutions was obtained (see Table) which could be explained rationally if the largest g was g_z, the lowest g was g_y, and g_x was negative. This yielded values of A *ca.* (0.8—0.9) ±0.001, B *ca.* (0.4—0.6) ±0.001, C *ca.* (0—0.1) ±0.001, k *ca.* (1.1—1.25) ±0.007, $6\epsilon/\xi$ *ca.* (0.06—0.1) ±0.005, E/ξ *ca.* 1 ±0.001, and Δ/ξ *ca.* (−0.1 to −0.7) ±0.015.

The most important general conclusion is that the $d_{x^2-y^2}$ energy level lies below the $d_{xz,yz}$ pair which are themselves split to an extent which in the majority of cases is greater than the tetragonal splitting parameter Δ (*i.e.* $6\epsilon/\Delta > 1$). The orbital-reduction factor slightly exceeds 1 and is relatively constant suggesting that the magnetic structures of the complexes are similar and consistent with expectation.[10] The average excitation energy is close to the spin–orbit coupling parameter and shows that mixing of excited states is very important for a full understanding of the structure and bonding in these complexes.

The orbital-reduction factor, k, decreases in the complexes *trans*-$[Ru(en)_2X_2]^+$ in the order X = Cl > Br > I > SCN, in dmf, dmso, and hmpa, but in water the trend is Cl ≈ Br < I ≈ SCN. In *trans*-$[Ru(dadn)X_2]^+$, in all solvents, the trend is always Cl < Br. These irregularities remind us that the parameter k is a sink into which covalency and any other unaccounted effects are drawn [15] and little can be concluded from it.

Much more useful information can be deduced from the crystal-field parameters Δ and 6ϵ and their ratio $6\epsilon/\Delta$ which gives information about the rhombicity of the complex. The strong axial crystal field coupled with a negative Δ resulting in the energy-level order given in Figure 2, *i.e.* $d_{x^2-y^2} < d_{xz,yz}$, is readily explained by an axial compressive distortion to the crystal field arising from the weaker σ bonding between Ru and Cl relative to N. Furthermore, Cl→Ru π bonding must be small since such π bonding would tend to destabilise the non-bonding $d_{xz,yz}$ pair of orbitals. In *trans*-$[Ru(en)_2X_2]^+$, *trans*-$[Ru(cyclam)Cl_2]^+$, and *trans*-$[Ru(dadn)X_2]^+$ there is a strong axial crystal field in which for X = Cl the trend in Δ is cyclam > dadn > en for each of the solvents dmf, H_2O, dmso, and hmpa. The variation in Δ for the different halide complexes in the family *trans*-$[Ru(en)_2X_2]^+$ depends upon the solvent and the factors controlling this are not easy to quantify. The values of Δ for different halides in the four different solvents are shown in Figure 4. These trends are explained by the strong electrostatic interaction between the donating O atom in H_2O and the halogens in the complex compared with the weak solvating power of dmf, hmpa, and dmso towards halogens. Since a strong solvent interaction between the halogen and the solvent would weaken the bond between Ru and halogen, then a weakening of the σ bond would lower Δ, but a weakening of the π bond would

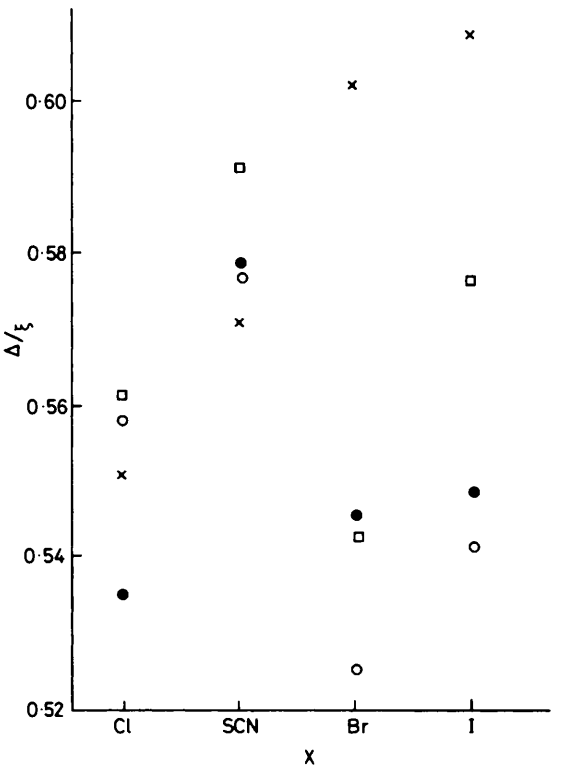

FIGURE 4 The values of Δ/ξ for the complexes *trans*-$[Ru(en)_2X_2]^+$ in dmf (□), dmso (○), H_2O (×), and hmpa (●) for X = Cl, Br, I, or SCN

increase Δ. Because water strongly solvates halogens it would be expected consistently to cause the complex to have a much smaller Δ value if the ruthenium–halide σ bond is so weakened. However, in all the complexes, H_2O results in a much higher value of Δ than expected, and this shows that the oxygen of the water is interacting (more so than the other solvents) and drawing charge from the π orbitals on the halogen, thus weakening the Ru–X π bond and causing Δ to increase. The overall change in Δ for the complexes in water (Cl < SCN < Br < I) also is accounted for by the general weakening of solvation through the series of these halogens. This order is the reverse of that expected from ligand-field theory in unsolvated complexes and shows the influence of solvent in these cases.

Another effect of uncertain importance is the solvation of the equatorial ligands by the hydrophobic ends of the solvent molecules. A strong interaction will weaken the Ru–N bonds and cause Δ to increase.

After a period of time, solvolysis takes place and halogens are progressively displaced by solvent molecules so that the species $[RuL_4X(solv)]^{2+}$ and $[RuL_4(solv)_2]^{3+}$ are formed in each solvent. For the monosubstituted complexes, the order of Δ for each halide complex was dmso > dmf > hmpa > H_2O and this follows the expected order of strength of crystal field of these solvents as ligands. In the disubstituted complexes, the value of Δ for any one solvent was dependent upon the parent halide. This result is curious and suggests some form of residual ion pairing affecting the g tensors despite attempts to remove all the halide. The differences in Δ are not great (especially for dmso, H_2O, and hmpa) and may well be no more than experimental error.

The rhombic distortion parameter 6ε varies widely, and rather irregularly. The most important observation is the large value of the ratio $6\varepsilon/\Delta$. A value of 0.67 implies equally spaced d_{yz}, d_{xz}, $d_{x^2-y^2}$. Values larger than this show that the crystal field along the x or y axes is stronger than that along z. This is particularly true in the mono- and di-substituted complexes and the *cis* isomers. Some general trends are, however, evident. For any one solvent in *trans*-$[Ru(en)_2X_2]^+$, the order of 6ε in most cases is I > Br > SCN > Cl. This could be explained by asymmetric solvation of the more polarisable larger halides causing the effective ligand field along x and y to be exaggerated.

It is gratifying that the deduced parameters are so similar to those found by Sakaki *et al.*[5] in $[Ru(NH_3)_5X]Cl_2$ (X = Cl, Br, or I).

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REFERENCES

[1] See for example, J. A. Broomhead and L. A. P. Kane-Maguire, *Inorg. Chem.*, 1968, **7**, 2519; 1971, **10**, 85; J. A. Broomhead, L. A. P. Kane-Maguire, and D. Wilson, *ibid.*, 1975, **14**, 2575.
[2] R. E. de Simone, *J. Am. Chem. Soc.*, 1973, **95**, 6238.
[3] N. J. Hill, *J. Chem. Soc., Faraday Trans. 2*, 1972, 427.
[4] A. Hudson and M. J. Kennedy, *J. Chem. Soc. A*, 1969, 1116.
[5] S. Sakaki, N. Hagwara, Y. Yanase, and A. Ohyoshi, *J. Phys. Chem.*, 1978, **82**, 1917.
[6] O. K. Medhi and U. Agarwala, *Inorg. Chem.*, 1980, **19**, 1381.
[7] P. T. Manoharan, P. K. Mehrotra, M. M. Taqui Khan, and R. K. Andal, *Inorg. Chem.*, 1973, **12**, 2753.
[8] C. K. Poon and D. A. Isabirye, *J. Chem. Soc., Dalton Trans.*, 1977, 2115.
[9] L. A. P. Kane-Maguire and G. Thomas, *J. Chem. Soc., Dalton Trans.*, 1975, 1324.
[10] J. S. Griffith, *Mol. Phys.*, 1971, **21**, 135.
[11] J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, 1961, pp. 364—373.
[12] J. H. M. Thornley, *Proc. Phys. Soc. London C*, 1968, **1**, 1024.
[13] G. M. Harris Loew, *Biophys. J.*, 1970, **10**, 196.
[14] National Algorithms Group (NAGLIB), program C05NAF.
[15] J. M. Baker, B. Bleaney, and K. D. Bowers, *Proc. Phys. Soc. London B*, 1956, **69**, 1205; B. Bleaney and M. C. B. O'Brien, *ibid.*, p. 1216; M. Gerloch and J. R. Miller, *Prog. Inorg. Chem.*, 1968, **10**, 1.