

Electron spin resonance studies of distorted octahedral ruthenium(III) species

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Abstract. The g -tensor theory of low-spin d^5 configuration in octahedral fields having axial (tetragonal or trigonal) and rhombic distortions is summarised. Illustrations taken from literature concern the following ruthenium(III) species: $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ (trigonal), $\text{Ru}(\text{bpy})_3^{3+}$ (trigonal), the Creutz-Taube cation (axial + rhombic) and $\text{RuCl}_2(\text{HL})(\text{L})$ (axial + rhombic; HL = isonitrosoketone). The rationalisation of distortion parameters in terms of bonding is considered.

Keywords. Ruthenium; distortion parameters; electron spin resonance.

1. Introduction

Electron spin resonance studies of low-spin d^5 ions in grossly octahedral environments were initiated nearly three decades ago and it has continued to be an area of significant activity through the years. One reason for this is no doubt the widespread interest in the compounds of iron(III) and ruthenium(III) which span the d^5 configuration. Historically the first-ever observation of ligand hyperfine in ESR was made by Owen and Stevens (1953) in the low-spin d^5 ion IrCl_6^{2-} . Significant distortion from cubic symmetry were noted by Baker *et al* (1956) and Bleaney and O'Brien (1956) in $\text{Fe}(\text{CN})_6^{3-}$ —an ion often considered to be ideally octahedral. The evaluation of the nature and extent of the subtle distortions of grossly octahedral environments has indeed been a focal point in ESR studies of low-spin d^5 ions.

In this article we examine the ESR parameters of a few pseudooctahedral ruthenium(III) complexes after briefly overviewing the theory of low-spin d^5 g -tensors. It is more of a short personal account of an area where our interest has grown in recent years.

2. Theory

In octahedral geometry, the 2T_2 ground term for low-spin d^5 species arises from the configuration t_2^5 (contributions from excited states are ignored for the present). The g -tensor theory of this configuration was developed by Bleaney and O'Brien (1956) and by Griffith (1961) in the framework of hole formalism. We shall follow the direct five-electron approach of Hill (1972) in a modified form.

A general distortion of the octahedron is expressed as the sum of axial and rhombic distortion. The axial distortion which can be tetragonal (or trigonal) splits the one-

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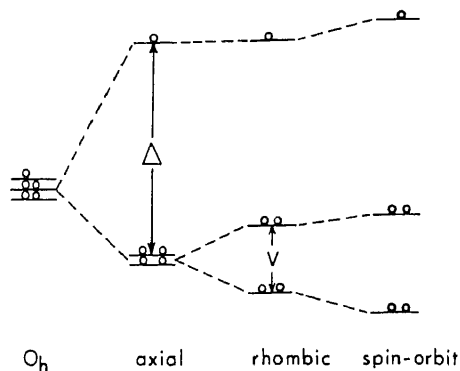


Figure 1. Splitting of t_2 level due to distortions and spin-orbit coupling.

electron t_2 representation into \mathbf{b} (or \mathbf{a}) and \mathbf{e} representations (small letters are used for one-electron representations and capital letters for state representations). The rhombic component splits \mathbf{e} further into two nondegenerate orbitals. This is illustrated in figure 1. The axial splitting parameter Δ is defined to be positive when \mathbf{b} (or \mathbf{a}) lies above \mathbf{e} as in figure 1. In the d^5 system the spin-orbit coupling parameter (λ) is positive.

The three one-electron t_2 functions can be constructed from the spherical harmonics Y_2^m (Sugano *et al* 1970) in a manner compatible with the anticipated distortion. The six five-electron functions corresponding to the 2T_2 state are obtained by populating these base functions. In tetragonal (or trigonal) symmetry the states span the representations B (or A), and E (consisting of E_+ and E_-) each with either α or β spin. For Δ positive, the configuration $\mathbf{e}^4\mathbf{b}^1$ (or $\mathbf{e}^4\mathbf{a}^1$) is lower in energy than $\mathbf{e}^3\mathbf{b}^2$ (or $\mathbf{e}^3\mathbf{a}^2$) and consequently the nondegenerate state B (or A) lies lower than E . The case E below B (or A) corresponds to negative Δ . In the presence of rhombic distortion, the E representation is no longer appropriate. However we shall continue to use the E_+ and E_- labels even in rhombic cases to stress the parenthood of the states so labelled.

For visualisation, the one-electron base functions of table 1 can be combined to afford the d -orbitals in familiar real forms. In a tetragonal system with z as the tetragonal axis, d_{xy} lies above d_{xz} , d_{yz} when Δ is positive and d_{yz} lies above d_{xz} when the added rhombic splitting V is positive. In a trigonal system (z is the trigonal axis here) Δ is positive when d_{z^2} lies highest. The two other orbitals are respectively linear

Table 1. The t_2 functions in tetragonal and trigonal situations.

Function		Representation
Tetragonal	Trigonal	
$\frac{1}{\sqrt{2}}(Y_2^2 - Y_2^{-2})$	Y_2^0	$\mathbf{b(a)}$
Y_2^{-1}	$-(\sqrt{2}Y_2^{-2} + Y_2^1)/\sqrt{3}$	\mathbf{e}_+
$-Y_2^1$	$(\sqrt{2}Y_2^2 - Y_2^{-1})/\sqrt{3}$	\mathbf{e}_-

Table 2. The energy matrix.

		$ E_- \rangle$	$ \bar{B} \text{ (or } \bar{A}) \rangle$	$ E_+ \rangle$
		$ \bar{E}_+ \rangle$	$ B \text{ (or } A) \rangle$	$ \bar{E}_- \rangle$
$ E_- \rangle$	$ \bar{E}_+ \rangle$	$2\Delta + \lambda/2$	0	$V/2$
$ \bar{B} \text{ (or } \bar{A}) \rangle$	$ B \text{ (or } A) \rangle$	0	Δ	$-\lambda/\sqrt{2}$
$ E_+ \rangle$	$ \bar{E}_- \rangle$	$V/2$	$-\lambda/\sqrt{2}$	$2\Delta - \lambda/2$

combinations of $d_{x^2-y^2}$ with d_{xz} and d_{xy} with d_{yz} and for positive V the former lies above the latter.

Under the combined effects of Δ , V and λ the six 2T_2 functions split into three Kramers doublets represented by two identical 3×3 matrices, as shown in table 2. States with β -spin are identified by putting a bar on top. The form of the matrix in table 2 is independent of the precise nature of the distortion.

The ground Kramers doublet is in equation (1) where the coefficients a , b and c (not to be confused with symmetry labels **a** and **b** of one-electron

$$\psi_1 = a|E_+ \rangle + b|\bar{B} \text{ or } \bar{A} \rangle + c|E_- \rangle, \quad (1a)$$

$$\psi_2 = a|\bar{E}_- \rangle + b|B \text{ or } A \rangle + c|\bar{E}_+ \rangle, \quad (1b)$$

orbitals used earlier) are real and depend on Δ , V and λ . In strict octahedral symmetry $a = \sqrt{2/3}$, $b = \sqrt{1/3}$ and $c = 0$. The three components of the g -tensor arise as matrix elements of $\beta H(2S + kL)$ within the two states and are stated in equations (2a)–(2c), where k is the orbital

$$g_x = 2[-2ac - b^2 - \sqrt{2kb}(a+c)], \quad (2a)$$

$$g_y = 2[2ac - b^2 - \sqrt{2kb}(a-c)], \quad (2b)$$

$$g_z = 2[-a^2 + b^2 - c^2 - k(a^2 - c^2)], \quad (2c)$$

$$a^2 + b^2 + c^2 = 1, \quad (3)$$

reduction factor assumed to be isotropic. The normalization condition for coefficients is in equation (3). Changing the signs of any two of the equations among (2a)–(2c) corresponds to a mere rotation by π radian around an axis and leaves the physical results unaffected (Abragam and Bleaney 1970). The signs as chosen in equations (2a)–(2c) afford identical (in sign and magnitude) g_x and g_y in the axial case ($c = 0$).

The true orbital reduction factor should necessarily be less than 1. The actual value of k derived from experimental results with the help of (2)–(3) is often > 1 due to the presence of unaccounted effects. One of these effects is the admixture of the t_2^5 configuration with the excited configuration $t_2^4 e$ as shown by Thornley (1968) and Griffith (1971). Hill (1972) and Cotton (1972) have shown that this admixture can be accounted for by replacing k of (2) by the factor K as given by (4) where B is the Racah parameter and E_{av} is the average excitation energy of the $t_2^4 e$ configuration. In addition λ should be replaced by Λ as defined in (5).

$$K = (1 + 12B/E_{av})k, \quad (4)$$

$$\Lambda = \lambda(1 + \lambda/E_{av}). \quad (5)$$

In ruthenium(III) complexes $B \sim 600$, $\lambda \sim 1000$ and $E_{av} \sim 30000 \text{ cm}^{-1}$. Thus $K \sim 1.24 k$ and $\Lambda \sim \lambda$. Too much significance should not be attached to the values of k as indices of electron delocalisation.

3. Data processing

Given the signs and magnitudes of g_x , g_y and g_z , the parameters a , b , c , k , Δ/λ , V/λ as well as Kramers doublet eigenfunctions and eigenvalues can be found with the help of equations (2)–(4) and the matrix of table 2. In practice, the ESR experiment provides only the magnitudes of the three principal g values (g_1 , g_2 and g_3). Neither their sign nor their correspondence to g_x , g_y and g_z are known. There are therefore fortyeight possible combinations. Some of these are physically equivalent. Thus by permuting g_1 , g_2 and g_3 in the slots of g_x , g_y and g_z having fixed signs, a set of six correspondences can be generated which differ in some or all of the parameters a , b , c , Δ/λ and V/λ but which are physically equivalent and have the same value of k and relative energies of the Kramers doublets. The fortyeight possible combinations are aggregates of eight such sets each having six combinations. Hence by the choice of a suitable axes system and a correspondence (this is easily achieved in single crystal work with substances of known crystal structure) between g_1 , g_2 , g_3 and g_x , g_y , g_z (say, $g_1 = g_x$, $g_2 = g_y$ and $g_3 = g_z$) only eight alternatives differing in the signs of one or more g 's remain to be considered. Not all of these are physically meaningful and the value of K is often used as the criterion of acceptability. In most cases one is left to choose one from two alternatives which differ in the sign of one of the three g 's. Relatively simple programmes (Hudson and Kennedy 1969; Sakaki *et al* 1978) can be devised to compute upto this stage. The final choice is usually made by considering several factors including the sign and magnitude of Δ . The most powerful discriminator is, however, the energetics of the optical transitions from the ground Kramers doublet to the excited ones ($\Delta E_1/\lambda$ and $\Delta E_2/\lambda$). Unfortunately such transitions are not always observable.

4. Examples

In the following sections we examine the ESR data of four pseudo-octahedral ruthenium(III) species in terms of distortion and other parameters discussed above. The chemical importance of the species chosen is delineated in each case. Trigonal and tetragonal situations are considered. The ESR g -values have been taken from the literature. Since different authors often process their data using different formalisms and sign conventions for parameters, we have, for the sake of consistency, reprocessed all data in terms of equations (2)–(4) and the matrix of table 2. Our discussion is based on parameters so derived.

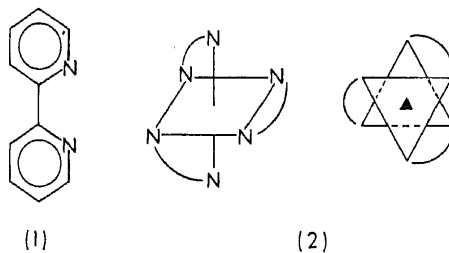
4.1 Hexaaquoruthenium(III) cation, $Ru(H_2O)_6^{3+}$

Well-characterised aquo ions of $4d$ and $5d$ elements are sparse in sharp contrast to those of the $3d$ metals. The low-spin $Ru(H_2O)_6^{3+}$ ion is thus of special interest. Bernhard *et al* (1984) has reported both single crystal and powdered ESR spectra of the cation doped into the alum $CsGa(SO_4)_2 \cdot 12H_2O$. The alum has a β -type structure (Beattie *et al* 1981) with the $M(H_2O)_6^{3+}$ octahedra showing a small trigonal distortion along the crystallographic $[111]$ axis.

The X-band ESR spectrum of the polycrystalline alum doped with 3% $^{101}\text{Ru}(\text{H}_2\text{O})_6^{3+}$ clearly reflects the axial distortion: $|g_z| = |g_{\parallel}| = 1.489$ and $|g_x| = |g_y| = |g_{\perp}| = 2.514$. From angular dependence of the g values of a rotated crystal it is concluded that the g axis coincides with the $[111]$ crystal axis. The hyperfine coupling of the electron spin with ^{101}Ru nucleus ($I = 5/2$) produces six equally spaced lines in the g_{\parallel} region with $|A_{\parallel}| = 2 \times 10^{-3} \text{ cm}^{-1}$. Splitting in the g_{\perp} region is unobserved due to line-width and it is estimated that $|A_{\perp}| \sim 1 \times 10^{-4} \text{ cm}^{-1}$. Interestingly the hyperfine splitting constants for $^{101}\text{Ru}(\text{H}_2\text{O})_6^{3+}$ are reduced by at least a factor of two compared to those of $^{101}\text{Ru}(\text{NH}_3)_6^{3+}$. One reason for this is believed to be the $p\pi-d\pi$ interaction (Bottcher *et al* 1979) between oxygen lone pairs and metal t_2 orbitals. The spin-density thus gets delocalised onto the aquo ligand. This cannot happen in the case of the amine complex. The results of processing the g values are in table 3. Two possible solutions differing in the signs of g_z exist. Solution 1 has larger K but smaller Δ/λ , $\Delta E_1/\lambda$ and $\Delta E_2/\lambda$. Using $\lambda \sim 1000 \text{ cm}^{-1}$, the Δ values of solutions 1 and 2 are ~ 350 and $\sim 2500 \text{ cm}^{-1}$ respectively. Since experimental information on ΔE_1 and ΔE_2 is lacking, only a tentative choice can be made between the two solutions. Bernhard *et al* (1984) has reported only the first solution with no explicit mention of the second solution and their axial parameter is negative (-350 cm^{-1}) apparently due to a different sign convention. Since the trigonal distortion of the $\text{M}(\text{H}_2\text{O})_6^{3+}$ ions in β -alums is of a minor nature in the crystallographic sense the first solution with $\Delta \sim 350 \text{ cm}^{-1}$ is probably appropriate. The sign of Δ is positive meaning that the A state lies below the E state. The $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ ion doped in β -alum is a model example of weak trigonal distortion. The K value of solution 1 affords $k = 1.15/1.24 = 0.93$.

4.2 Tris(2,2'-bipyridine)ruthenium(III) cation, $\text{Ru}(\text{bpy})_3^{3+}$.

The bpy complexes of ruthenium are of considerable current interest in relation to photochemical sensitisation and catalysis. The electronic structure of $\text{Ru}(\text{bpy})_3^{3+}$ (2) is of relevance in this context. The powder ESR spectrum of this complex (PF_6^- salt in a diamagnetic host lattice) was reported and analysed by DeSimone and Drago (1970). Confusion regarding the signs of parameters had prompted a reanalysis (Kober and Meyer 1983).



The $\text{Ru}(\text{bpy})_3^{3+}$ ion had D_3 symmetry and provides a good example of trigonal distortion brought about by tris chelation of a symmetrical bidentate ligand. The observed ESR spectrum is axial (table 3) and it is presumed that $g_z (= g_{\parallel})$ coincides with the C_3 axis. The g values permit two solutions for the parameters (table 3). By a systematic comparison of the ESR spectra of $\text{Fe}(\text{bpy})_3^{3+}$, $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Os}(\text{bpy})_3^{3+}$ Kober *et al* (1983) concluded that solution 1 is correct. The similarity in the ESR characteristics of the ions $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ is noteworthy.

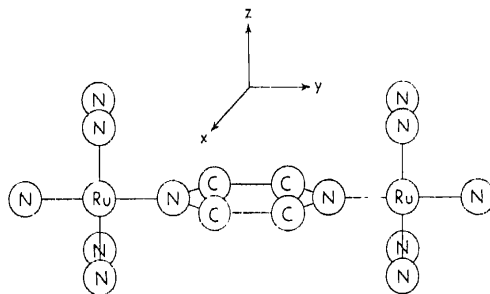
Table 3. The g -values and derived parameters.

Compound	Solution No.	g_x	g_y	g_z	a	b	c	K	Δ/λ	V/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$
$[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$	(1)	-2.514	-2.514	-1.489	0.743	0.668	0.000	1.152	0.348	0.000	1.422	1.635
	(2)	-2.514	-2.514	1.489	0.298	0.954	0.000	0.858	2.535	0.000	2.478	3.256
$[\text{Ru}(\text{bpy})_3]^{3+}$	(1)	-2.640	-2.640	-1.140	0.705	0.708	0.000	1.156	0.507	0.000	1.414	1.710
	(2)	-2.640	-2.640	1.140	0.382	0.923	0.000	0.932	1.912	0.000	1.999	2.705
$[(\text{NH}_3)_5\text{Ru}(\text{pz})\text{Ru}(\text{NH}_3)_5]^{5+}$	(1)	-2.799	-2.487	-1.346	0.723	0.690	0.030	1.198	0.436	-0.138	1.409	1.687
	(2)	-2.799	-2.487	1.346	0.330	0.943	0.040	0.981	2.314	-0.734	2.171	3.201
$\text{RuCl}_2(\text{HL})(\text{L})$	(1)	-2.470	-2.470	-1.849	0.774	0.632	0.000	1.2057	0.210	0.000	1.444	1.577
	(2)	-2.470	-2.470	1.849	0.153	0.988	0.000	1.2055	4.943	0.000	4.663	5.553

Since the sign of Δ is positive the ground state has A_1 symmetry (D_3 point-group). This can be rationalised in molecular orbital terms. The HOMO (π) and LUMO (π^*) orbitals of the $(\text{bpy})_3$ ensemble span the representatives $a_1 + e$ and $a_2 + e$ respectively. The metal d orbitals of t_2 types span $a_1 + e$ and energetically these are intermediate between the π and π^* orbitals. Thus the $e(d)$ orbital is stabilized by interaction with $e(\pi^*)$ but destabilized by interaction with $e(\pi)$. The $a_1(d)$ orbital is destabilized by mixing with $a_1(\pi)$ but there is no stabilising mixing. Consequently $a_1(d)$ lies higher than $e(d)$. The five-electron ground state is thus $e(d)^4 a_1(d)^1$ which has A_1 symmetry.

4.3 The Creutz-Taube complex

Of fundamental importance in relation to our understanding of valence delocalisation, intervalence excitation and related phenomena is the model mixed-valence complex cation (μ -pyrazine) decamminediruthenium(II, III), $[(\text{NH}_3)_5\text{Ru}(\text{pz})\text{Ru}(\text{NH}_3)_5]^{5+}$, (3) called the Creutz-Taube complex (Creutz 1983). The electronic structure



(3)

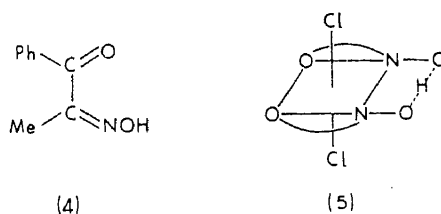
of the complex has been probed by different workers using the ESR tool (Hush *et al* 1980; Bunker *et al* 1978). Very recently a detailed single crystal work on $[(\text{NH}_3)_5\text{Ru}(\text{pz})\text{Ru}(\text{NH}_3)_5]\text{Cl}_5 \cdot 5\text{H}_2\text{O}$ at 3 K has appeared (Stebler *et al* 1984) and we consider this below. Here we have a case of tetragonal-cum-rhombic distortion. Crystal structure work has shown that the two ruthenium atoms in the above complex are structurally equivalent. The angle between the pyrazine plane and the *cis*- NH_3 -Ru bonds is 45° . The symmetry of the complex (ignoring protons) is C_{2h} . The overall ESR spectrum is rhombic and the following correspondence is established from angular dependence of g values measured with magnetic field along the crystallographic c -axis or in the ab plane: $|g_x| = 2.799$, $|g_y| = 2.487$ and $|g_z| = 1.346$. The molecular axes system shown in (3) is as follows: x , in the plane of the pyrazine ring but perpendicular to the Ru-Ru axis; y , the *trans*- NH_3 -Ru-N(pz) axis and z , perpendicular to the pyrazine ring. This axes system chosen to afford $|g_x| > |g_y| > |g_z|$ is different from that of Stebler *et al* (1984). The two possible solutions are in table 3. Both have positive Δ corresponding to a B ground state. Stebler *et al* (1984) considered only solution 2. They assign a broad band at about 2000 cm^{-1} in the infrared as the lower (ΔE_1) of the two transitions among the Kramers doublets. In solution 1 the transition energies are less but the margin is not wide enough to ignore this solution. This ambiguity remains.

In the axis system chosen, the tetragonal distortion occurs along the x axis and the unpaired electron is localised in an orbital of yz symmetry which is parallel to the π^* orbital of the pyrazine ring. The two sets of orbitals can interact and lead to delocalisation of the unpaired electron among the ligand and the metal atoms. The

value of the orbital reduction factor k (0.79, solution 2) is in line with such a delocalisation. Examination of the ESR spectra of crystals having ^{101}Ru isotopes failed to resolve any metal hyperfine splitting due to relatively large line-widths. No quantitative measure of the extent of delocalisation can therefore be offered from the ESR data.

4.4 *Trans-Ru(HL)(L)Cl₂*

The isonitroketones afford an interesting class of hydrogen-bonded ruthenium(III) species having the trans-RuX_2 ($\text{X} = \text{Cl}^-$, Br^-) moiety (Chakravarty and Chakravorty 1982). A particular example is (5) abbreviated as Ru(HL)(L)Cl_2 . The effective ESR symmetry of polycrystalline (5) is axial (table 3). The two possible solutions in this case



have nearly equal K values but widely different Δ/λ , $\Delta E_1/\lambda$ and $\Delta E_2/\lambda$. The complex displays a weak transition near 5000 cm^{-1} assignable to ΔE_1 and/or ΔE_2 (Bhattacharya and Chakravorty 1984). This means that solution (2) is correct.

The positive sign and relatively large value of Δ is easy to understand. We identify the Cl-Ru-Cl line as the axis of tetragonal distortion. Since Cl is below N and O in the spectrochemical series, the t_2 level will naturally split placing **b** above **e**. The e orbital (d_{xz} , d_{yz}) can be further stabilized by interaction with π^* orbitals of the (HL) (L) moiety but this stabilisation is unavailable for the d_{xy} orbital. We thus have a relatively large separation between **b** and **e**.

5. Concluding remarks

The purpose of this article has been to illustrate the use of ESR data in the hands of chemists for elucidating the electronic structure of some interesting ruthenium(III) compounds (the choice here is entirely subjective). Distorsion from idealised octahedral geometry is more or less the observed rule—be the distorsion due to crystal packing forces, ligand asymmetry or electronic factors. Magnetic distorsion is not necessarily an expression of geometric distorsion. Thus in the Creutz-Taube complex the geometric distorsion is along the $\text{H}_3\text{N-Ru-N(pz)}$ axis, yet the pseudo-tetragonal magnetic axis lies elsewhere. The nature and extent of axial and rhombic distorsions can be assessed from the experimental g values in terms of a simple theory. The ambiguity associated with two possible solutions can be resolved in most cases in one way or another. The result can then be translated in terms of orbitals and bonding.

Acknowledgement

Financial assistance received from the Department of Science and Technology and the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged.

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