related with steric interaction between the released chloride and the number of axial methyl groups,[26] while the rate increase due to ring expansion has been attributed to steric interaction of boat or twist-boat ring conformations.[1,27] The rate increase in the primary hydrolysis of *trans*-Co(en)-(tmd)Cl₂⁺ relative to *trans*-Co(en)₂Cl₂⁺ can also be accounted for on this basis and the positive value for the entropy of activation supports Tobe's theory,[24] as considerable stereochemical change is observed.

Registry No. [Cr(en)(tmd)Cl₂] ClO₄, 36904-25-3; *cis*-[Cr-

(26) M. D. Alexander, *Inorg. Chem.*, **5**, 2084 (1966).
(27) M. C. Couldwell and D. A. House, *Inorg. Nucl. Chem. Lett.*, **7**, 947 (1971).

(en)₂Cl₂]Cl·H₂O, 20713-30-8; [Cr(en)(tmd)(OH₂)OH] ClO₄, 36904-26-4; [Co(en)(tmd)Cl₂]Cl·H₂O, 36900-74-0; [Co(en)-(tmd)Cl₂]ClO₄, 36904-27-5; *trans*-Cr(en)(tmd)(OH₂)Cl²⁺, 36904-28-6; *cis*-Co(en)(tmd)(OH₂)Cl²⁺, 36904-29-7; *trans*-Cr(en)(tmd)(OH₂)₂³⁺, 36904-30-0; *cis*-Cr(en)(tmd)(OH₂)₂³⁺, 36904-31-1; *cis*-Co(en)(tmd)(OH₂)₂³⁺, 36904-32-2; *trans*-Co-(en)(tmd)(OH₂)₂³⁺, 36904-33-3; *trans*-Co(en)(tmd)(OH)₂⁺, 36904-34-4; Cr(tmd)(OH₂)₄³⁺, 36965-94-3.

Trigonal Field Splitting in Tris(ethylenediamine) Complexes. Evidence from the Electron Paramagnetic Resonance Spectrum of Ru(en)₃³⁺

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The epr spectrum of the tris(ethylenediamine)ruthenium(III) complex, Ru(en)₃³⁺, was measured at 4°K, diluted in single crystals of [Rh(en)₃Cl₃]₂·NaCl·6H₂O and in powders of [Co(en)₃]Br₃·3H₂O, and employing K-band and X-band frequencies, respectively. The spectrum in both media can be described by an axial spin Hamiltonian with $g_\perp = 2.640 \pm 0.022$ and $g_\parallel = 0.330 \pm 0.007$, defined with respect to the threefold symmetry axis of the complex. Interpretation of these g factors in terms of the theory of axial distortions for a low-spin d⁵ electronic configuration shows the ground electronic state to be E′(²A₁) and yields a value of the trigonal field splitting parameter, K, of −413 cm⁻¹. The observed magnitude and sign of this latter quantity are discussed in terms of the known structure of the complex, crystal field theory predictions, and a comparison with the value for the same quantity in other tris(ethylenediamine) complexes.

Introduction

For a transition metal ion immersed in a crystal field of predominantly octahedral symmetry, but with a superimposed component of trigonal (D_3) symmetry, the lower lying, triply degenerate (t_{2g}) set of d orbitals is expected to split into a nondegenerate a_1 orbital and a doubly degenerate set of e orbitals. Neglecting mixing with the higher energy set of e (e_g) orbitals, the energies of the split t_{2g} orbitals can be parametrized *via* crystal field theory as $E(e) = K$ and $E(a_1) = -2K$, where K, the trigonal field splitting parameter, characterizes the strength of the field.[1] For K positive, the a_1 orbital lies lowest.

For a number of trigonal complexes[2] and trigonal sites in ionic crystals[3] the magnitude and sign of K can be estimated from the splitting of excited electronic states as measured by polarized crystal spectra. However for the tris(ethylenediamine) complexes thus far examined,[4-7] the observed broadband splittings have been so slight, and their direct interpre-

tation complicated by the apparent additional presence of vibronic contributions to band intensities, that estimates of the magnitude of K obtained therefrom may still have a high degree of uncertainty attached to them. Moreover the sign of K for these complexes, determined in this manner, even seems to be controversial by comparison with the sign deduced from circular dichroism studies, both natural and magnetically induced.[8,9]

In favorable cases, such as for metal ions with degenerate ground states in octahedral fields, electron paramagnetic resonance is an additional method which can provide a direct, and precise, determination of the strengths of axial components of a crystal field. The low-spin d⁵ Ru³⁺ ion has been shown to be an excellent probe in this regard and has been used extensively to characterize the axial field strengths in a number of well-known type complexes and ionic crystals including the tris(acetylacetonate) complex,[10] corundum,[11] the hexaammine[12] and halopentaammine complexes,[13] several garnets,[14,15] several phosphine complexes,[16] some tris-

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(5) A. G. Karipedes and T. S. Piper, *J. Chem. Phys.*, **40**, 674 (1964).
(6) R. Dingle and C. J. Ballhausen, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **35**, 1 (1967).
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(9) R. L. Russell and B. E. Douglas, *Inorg. Chim. Acta*, **3**, 426 (1969).
(10) H. S. Jarrett, *J. Chem. Phys.*, **27**, 1298 (1957).
(11) S. Geschwind and J. P. Remeika, *J. Appl. Phys.*, **33**, 3705 (1962).
(12) J. H. E. Griffiths, J. Owen and I. M. Ward, *Proc. Roy. Soc., Ser. A*, **219**, 526 (1963).
(13) J. A. Stanko, Ph.D. Thesis, University of Illinois, 1966.

(diimine) complexes,[17] and magnesium oxide.[18] In view of the existence of the tris(ethylenediamine)ruthenium(III) complex[19] we felt it worthwhile to examine its epr spectrum in hopes of obtaining an independent estimate of the magnitude and sign of the trigonal field in such complexes, insofar as this one is representative of the general class.

Experimental Section

The bromide salt of the tris(ethylenediamine) cation [Ru-(NH$_2$CH$_2$CH$_2$NH$_2$)$_3$]Br$_3$·xH$_2$O ($x \cong 2$) was prepared as described previously.[20,21] This was cocrystallized with the analogous, diamagnetic cobalt salt [Co(en)$_3$]Br$_3$·3H$_2$O[22,23] by cooling a nearby saturated solution containing the two salts in a 1:20 weight ratio, to 0°. This doped, polycrystalline sample was ground, sealed in a Pyrex capillary, and placed in a liquid helium filled dewar having a finger which could be easily inserted into a Varian, rectangular, X-band epr cavity, between the pole faces of a 10-kOe magnet.

For the single-crystal experiments, the chloride salt of the Ru(en)$_3^{3+}$ cation [Ru(en)$_3$]Cl$_3$·xH$_2$O ($x \cong 4$)[20,21] was doped into either of the diamagnetic, uniaxial hosts (±)[M(en)$_3$Cl$_3$]$_2$·NaCl·6H$_2$O, where M = Co^6 or Rh.[24] Crystals were grown by allowing acidic (pH 1) solutions containing the chloride salt of the ruthenium complex and the chloride salts of either Co(en)$_3^{3+}$ [25] or Rh(en)$_3^{3+}$,[26] along with excess sodium chloride, to evaporate in a refrigerated desiccator. The acid solution and low temperature were employed to retard the decomposition of the ruthenium complex which occurs upon standing in solution.[21]

For obtaining the single-crystal epr spectra, crystals of approximate dimensions 0.5 × 0.5 × 1.5 mm were glued on the end of a 75-cm Lucite rod 4 mm in diameter with their trigonal axis aligned, with the aid of a polarizing microscope, perpendicular to the rod axis. The end of the rod containing the crystal had previously been machined to fit through a 3-mm access port in the top of a cylindrical, K-band cavity submerged in liquid helium, between the pole pieces of a 15-kOe magnet. A calibrated dial assembly was affixed to the end of the rod, opposite the crystal. This arrangement permitted a full 360° rotation of the crystal in the plane perpendicular to the rod.

Initially, cobalt crystals grown from solutions 1 mole % in ruthenium were examined; however the combination of small crystal size necessitated by the cavity access design and possibly the low actual concentration of paramagnetic impurity in the crystals thwarted attempts to obtain a signal. Next, the rhodium diluent, which it was thought would more readily accept the ruthenium impurity into its lattice, was tried. In addition, solutions 5% or more in ruthenium were also used. Rhodium crystals grown from these latter solutions did yield the desired signals though they were relatively broad, no doubt due to the high concentration of paramagnetic species in the crystal.

Field measurements were made using a proton probe placed between the helium dewar assembly and the pole tips or in a few instances were read directly from the gaussmeter provided with the magnet. The magnitude of the difference between the field at this point and at the sample was estimated by several field measurements taken at the approximate center of the poles with the dewar removed. The klystron frequency was measured using a wavemeter.

Results

The epr spectrum of a powdered sample of the tris(ethylenediamine)ruthenium(III) complex diluted in the salt

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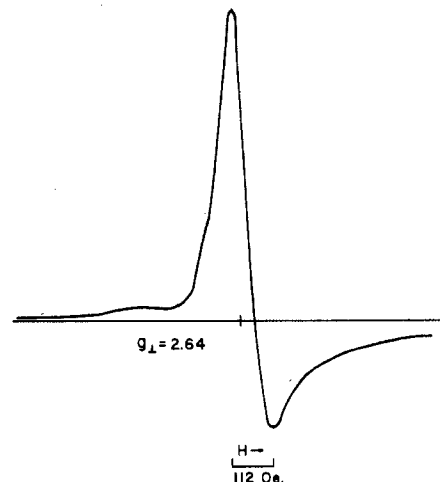
(26) F. Galsbol, *Inorg. Syn.*, **12**, 269 (1971).

Figure 1. Epr spectrum of Ru(en)$_3^{3+}$ in a powdered diamagnetic host, [Co(en)$_3$]Br$_3$·3H$_2$O, at 4°K. Klystron frequency was 9.2345 × 10^9 sec^{-1}.

Co(en)$_3$Br$_3$·3H$_2$O was examined initially. ter Berg[22] has shown this salt to be trigonal, space group P$\bar{3}$c1, with four cobalt ions per unit cell, at sites of C$_3$ symmetry. All the sites are magnetically equivalent since the C$_3$ axis of each is parallel to the c axis of the cell. Figure 1 shows the spectrum observed for this powder at 4°K and X-band frequency. It consists of a single asymmetric resonance line centered[27] at g = 2.646 ± 0.020 (H = 2493 Oe, ν = 9.2345 × 10^9 sec^{-1}), with a hint of fine structure on the low-field side of the resonance. For an S = $^1/_2$ ion in an axial crystal field the effective spin Hamiltonian is, neglecting metal–hyperfine interactions

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y)$$

and two resonances, associated with $g_{\parallel}$ and $g_{\perp}$, are to be expected in the spectrum of the polycrystalline material with the perpendicular component being considerably more intense than the parallel based on statistical considerations.[28] Since we observe no other resonance up to the field limit of our magnet (10 kOe) we assign the observed resonance to $g_{\perp}$ and assume that $g_{\parallel}$ must be less than 0.66.

The above interpretation of the spectrum of the polycrystalline sample was entirely confirmed by a single-crystal study of the Ru(en)$_3^{3+}$ complex diluted in the diamagnetic rhodium salt (±)[Rh(en)$_3$Cl$_3$]$_2$·NaCl·6H$_2$O, which has been used previously as a diluent for optical spectroscopy of the Co(en)$_3^{3+}$ cation.[24] Though there are no published crystallographic data on this rhodium salt, it grows as pseudohexagonal plates or needles which exhibit extinction and interference patterns in polarized light characteristic of uniaxial crystals. The analogous cobalt salt (±)[Co(en)$_3$Cl$_3$]$_2$·NaCl·6H$_2$O (which was also used here initially as a diluent; see Experimental Section) has been shown by X-ray diffraction to be trigonal, space group P$\bar{3}$c1, with four cobalt ions per unit cell at sites of C$_3$ symmetry and with the C$_3$ axes of all sites parallel to the c axis of the cell making them all magnetically equivalent. The sodium chloride double salt was chosen over the simple halide salts in view of its apparent fixed hydration number, since McGarvey,[29] in his epr study

(27) In the absence of computer simulation programs for powder spectra, the field position used to compute the g factor was taken to be the point on the asymmetric derivative curve at a height obtained by substracting the small negative deflection from the larger positive deflection. "g" estimated in this manner compares well with the more precise single-crystal value.

(28) J. A. Ibers and J. D. Swalen, *Phys. Rev.*, **127**, 1914 (1962).

(29) B. R. McGarvey, *J. Chem. Phys.*, **41**, 3743 (1964).

of the tris(ethylenediamine)chromium(III) complex, observed considerable line broadening in the simple halide salts compared to the sodium chloride salt and attributed it to low-symmetry electric fields produced by the partial occupancy of 12-fold sites about the cations by the water molecules in the cell. Herein we assume the NaCl double salt of the rhodium chloride salt to be isomorphous to the cobalt one.

A crystal of the rhodium salt grown from a solution 10 mole % in ruthenium (see Experimental Section) was mounted so it could be rotated in the epr cavity about an axis perpendicular to the trigonal axis of the crystal. For all orientations of the field with respect to the trigonal axis in the plane of rotation, only a single resonance line was observed. (This attests to the magnetic equivalency of all the metal sites in these crystals for this orientation.) This line reached its minimum field position when the applied field, H, was perpendicular to the trigonal axis of the crystal ($\theta = 90°$) and, hence, presumably to the C_3 molecular axis of the individual Ru(en)$_3$$^{3+}$ complexes. The line moved upfield rapidly as θ decreased, to beyond the magnet limit (15 kOe) as H approached parallelism with the trigonal axis. Table I and Figure 2 summarize the data obtained from the angular variation study in this orientation. Since the powder spectrum results indicated very little deviation from axial symmetry (*i.e.*, $g_x = g_y$) for the Ru(en)$_3$$^{3+}$ complex, angular variation studies in a plane perpendicular to the trigonal axis were not performed.

McGarvey[30] has shown that the effective single-crystal g value for an $S = \frac{1}{2}$ ion with a spin Hamiltonian of axial symmetry is given by the equation

$$g^2 = g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta$$

where θ is the angle between the z symmetry axis of the paramagnetic ion and the applied magnetic field H. This equation was recast into a form linear in $\sin^2 \theta$

$$g^2 = (g_\perp^2 - g_\parallel^2) \sin^2 \theta + g_\parallel^2$$

and the angular variation data of Table II fit to it using the least-squares technique. Tolerances of 0.003 and 0.01 were set for g^2 and $\sin^2 \theta$, respectively. This analysis yielded g factors for the complex of $g_\parallel = 0.330 \pm 0.007$ and $g_\perp = 2.640 \pm 0.022$, with the latter in good agreement with the powder estimate above, *viz.*, 2.646 ± 0.020.

The epr signals obtained from the doped single crystals were rather broad, with peak-to-peak half-widths ranging from a minimum of 100 Oe at θ near 90° to 350 Oe for θ near 30°, at the upper limit of the magnetic field attainable. This broadness, which is undoubtedly due to significant electronic dipolar interactions arising from the high Ru(III) concentrations in the crystals, prohibited the resolution of any hyperfine structure from the nuclear spin, $I = \frac{5}{2}$, isotopes, ^{99}Ru (12.8%) or ^{101}Ru (17.0%). However the fine structure resolvable in the polycrystalline spectrum, Figure 1, is probably due to such hyperfine interactions. A crude estimate of the hyperfine splitting constant B, associated with the $B(I_xS_x + I_yS_y)$ hyperfine term in the Hamiltonian, can be obtained by assigning the low-field shoulder on the $g_\perp$ resonance of the powder spectrum to the $M_I = \frac{5}{2}$ component. Then the field separation, 289 Oe, between it and the main zero nuclear spin resonance is just $10/4B$, which yields a B of 0.0143 cm^{-1}. This value is roughly 2-3 times the magnitude of the electron–nuclear hyperfine coupling con-

(30) B. R. McGarvey, *Transition Metal Chem.*, 3, 89 (1966).

Table I. Resonance Field as a Function of Crystal Orientation[a]

No.	θ,[b] deg	Field,[c] Oe	g[d]
1	81.5	6,114 (11)	2.617
2	86.5	6,069 (11)	2.637
3	88.5	6,050 (11)	2.645
4	83.5	6,084 (11)	2.630
5	78.5	6,186 (11)	2.587
6	73.5	6,322 (11)	2.531
7	68.5	6,495 (11)	2.464
8	63.5	6,757 (11)	2.368
9	58.5	7,131 (13)	2.244
10	48.5	8,012 (13)	1.997
11	38.5	9,517 (17)	1.681
12	33.5	10,885 (24)	1.470
13	28.5	12,441 (24)	1.286
14	23.5	14,716 (26)	1.087
15	−26.5	13,247 (24)	1.208
16	−31.5	11,366 (24)	1.408
17	−36.5	9,957 (17)	1.607

[a] Ru(en)$_3$$^{3+}$ in (±)[Rh(en)$_3$Cl$_3$]$_2$·NaCl·6H$_2$O. [b] θ is the angle which the applied field makes with the crystal C_3 symmetry axis. [c] The field values, H, for points 1-12 were obtained using a proton probe; for points 13-17 a gaussmeter was used. The number in parentheses is the estimated error in the measurement in oersteds. [d] $g = h\nu/\beta H$. The klystron frequency was 22.403 × 10^9 sec^{-1}.
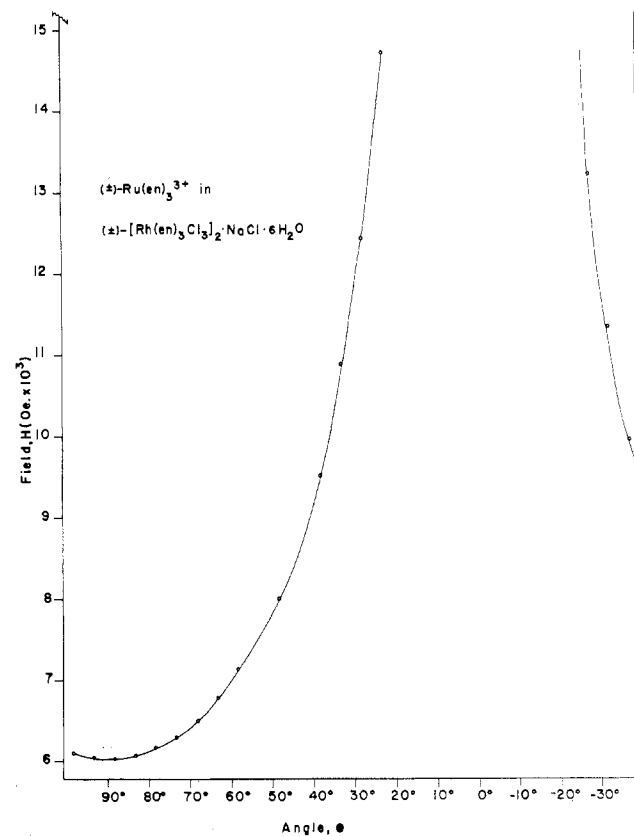

Figure 2. Plot of angular variation of epr spectrum (Table II) of Ru(en)$_3$$^{3+}$ in the single-crystal, uniaxial host (±)[Rh(en)$_3$Cl$_3$]$_2$·NaCl·6H$_2$O at 4°K and $\nu = 22.403 × 10^9$ sec^{-1}. θ is the angle between the magnetic field direction and the threefold axis of the crystal. The crystal was rotated about an axis perpendicular to the trigonal crystal axis.

stants for ^{99,101}Ru in the few other instances in which hyperfine splitting has been observed.[12-15,18]

Discussion

Miller and Offenbacher[14] have given a thorough theoretical analysis of the effect of a combined trigonal field and spin-orbit coupling perturbations on the ground $^2T_{2g}$ state arising from the t_{2g}^{5} electronic configuration of an octahedrally co-

Table II. Polar Angles[a] in $M(en)_3{}^{m+}$ Complexes

Oct	Cr^{III}	Co^{III}	Ni^{II}	Cu^{II}	Ru^{III}
54° 44′	56° 41′[b]	53° 32′[c]	55° 20′[f]	56° 46′[h]	57° 19′[i]
		54° 18′[d]	56° 26′[g]		
		55° 30′[e]			

[a] Where site symmetry was lower than D_3, the polar angle reported is the average of the individual polar angles of the M–N bonds relative to an axis coincident with the plane normal through the metal atom from the plane defined by three separate ring nitrogen atoms on either end of the complex. [b] [Cr(en)₃][Co(CN)₆]·6H₂O: K. N. Raymond and J. A. Ibers, *Inorg. Chem.*, 7, 2333 (1968). Note: cation in Λ(λλλ) configuration. [c] D-[Co(en)₃Cl₃]₂·NaCl·6H₂O: K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, 30, 158 (1957). [d] [Co(en)₃]Cl₃·3H₂O: K. Nakatsu, Y. Saito, and H. Kuroya, *ibid.*, 29, 428 (1956). [e] [Co(en)₃]₂[HPO₄]₃·9H₂O: E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, 10, 1486 (1971). [f] [Ni(en)₃](NO₃)₂: L. N. Swink and M. Atoji, *Acta Crystallogr.*, 13, 639 (1960). [g] [Ni(en)₃]SO₄: M. Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, 9, 2421 (1970). [h] [Cu(en)₃]SO₄: D. L. Cullen and E. C. Lingafelter, *ibid.*, 9, 1858 (1970). [i] [Ru(en)₃]Cl₃·3.5H₂O: ref 20.

ordinated Ru³⁺ ion. Their analysis treated the configuration as a single hole whereby the theoretical results for a $t_{2g}{}^1$ configuration were applicable once the associated sign changes of the trigonal field and spin-orbit coupling parameters K and ζ are made. Figure 3 summarizes these results for both the one-electron orbital energies and the state energies for the Ru³⁺ ion, for the two sign choices for the trigonal field, based on the diagonalization of the matrices of K and ζ^{14} within the $t_{2g}{}^5$ configuration, *i.e.*, neglecting configuration interaction. The symmetry group nomenclature for the double groups is that adopted by Griffith.[31]

As can be seen from Figure 3, for either of the possible signs for K, a Kramers doublet, E', is the ground state, thus affording the possibility of an observable magnetic resonance for the ion, albeit only at reduced temperatures due to the short spin–lattice relaxation times usually associated with this electronic configuration.

General expressions have been given by Stevens[32] and later by Kamimura[33] for the g factors of the E' ground states of the $t_{2g}{}^5$ configuration under an axial field and spin–orbit coupling perturbations. According to Stevens these are

$$g_{\parallel} = 2\,|(1 + k)\cos^2\alpha - \sin^2\alpha\,|$$

$$g_{\perp} = 2\,|\sqrt{2k}\,\cos\alpha\sin\alpha + \sin^2\alpha\,|$$

where $\tan 2\alpha = \sqrt{2}/(\tfrac{1}{2} + 3K/\zeta)$ and $0 < 2\alpha < \pi$, $-3K^{34}$ is the one-electron orbital energy difference $[E(a_1) - E(e)]$, as mentioned in the Introduction, and ζ is the spin–orbit coupling constant. k, the orbital reduction factor, incorporates the reduction, due to covalency effects, of the orbital angular momentum of the t_{2g} electron from a value of 1.0. Through these expressions, values of k and the ratio $3K/\zeta$ can be obtained from the observed g factors. If ζ is taken as positive, then K takes the sign derived for the ratio $3K/\zeta$ and will correspond to the desired one-electron value (Figure 3).

We display in Figure 4 the g factors $g_{\parallel}$ and $g_{\perp}$, computed from the above equations as a function of $3K/\zeta$ for two typical values of the orbital reduction factor, k. The curve for $k = 1.0$ is identical with that given earlier by Kamimura.[33]

(31) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, London, 1961, p 385.
(32) K. W. Stevens, *Proc. Roy. Soc., Ser. A*, 219, 542 (1953).
(33) H. Kamimura, *J. Phys. Soc. Jap.*, 11, 1171 (1956).
(34) In ref 32, the axial field parameter employed was designated as Δ and defined as the orbital energy difference $[E(a_1) - E(e)]$. In terms of our previously introduced nomenclature Δ = $-3K$. Another commonly used designation for the axial field parameter is v, and again $v = -3K$ in terms of the nomenclature used herein.
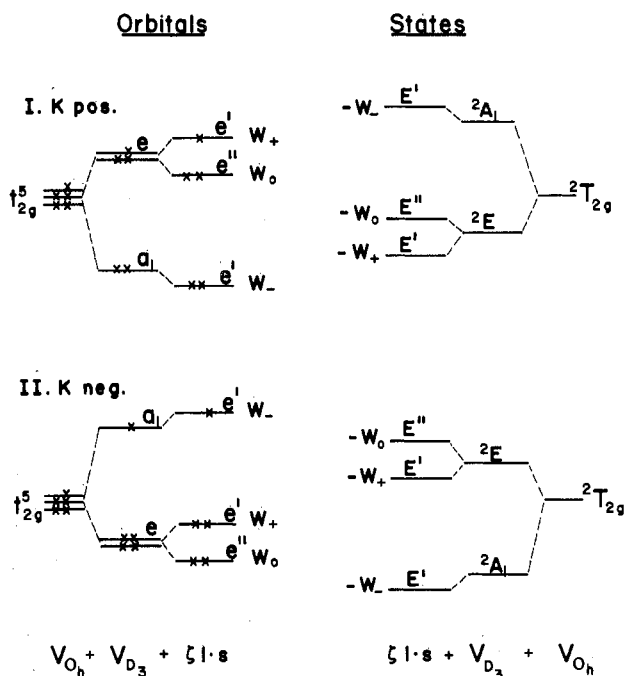
Orbitals

States

$$V_{O_h} + V_{D_3} + \zeta\,l\cdot s \qquad \zeta\,l\cdot s + V_{D_3} + V_{O_h}$$

Figure 3. One-electron d-orbital and state energy levels, W_i, for an octahedral $t_{2g}{}^5$ configuration in the presence of trigonal field and spin-orbit coupling perturbations, illustrated for the two possible sign choices for the trigonal field parameter K. The expressions for the one-electron matrix elements, from ref 14, are $\langle e|V_{trig} + \zeta l\cdot s|e\rangle = K + \zeta/2$, $\langle a_1|V_{trig} + \zeta l\cdot s|a_1\rangle = -2K$, and $\langle e|\zeta l\cdot s|a_1\rangle = \zeta/\sqrt{2}$. The energy expressions after diagonalization are $W_0 = K - \zeta/2$ and $W_{\pm} = \tfrac{1}{2}[-K + \zeta/2 \pm (9K^2 + 3K\zeta + 9/4\zeta^2)^{1/2}]$. For the Ru(en)₃³⁺ complex with $K = -418$ and $\zeta = 1050$ cm⁻¹, the actual energies become $W_0 = -943$ cm⁻¹, $W_+ = -336$ cm⁻¹, and $W_- = +1279$ cm⁻¹

once his differing definition of the trigonal field splitting parameter is allowed for. The observed g factors for the Ru(en)₃³⁺ complex of $g_{\parallel} = 0.330$ and $g_{\perp} = 2.640$ are only consistent with the right-hand side of Figure 4, *i.e.*, with negative values of the parameter $3K/\zeta$ and hence with a *negative* value of the trigonal field splitting parameter K.

From the observed negative sign of K we can immediately conclude that the energy ordering of the trigonal field split t_{2g} orbitals in the complex is e < a₁ (case II of Figure 3) and that the ground electronic configuration must be $e^4 a_1{}^1$ corresponding to a ²A₁ ground state (in the limit of $\zeta = 0$). The precise magnitudes of $3K/\zeta$ and k are obtained by fitting the observed g factors to curves similar to those in Figure 4. In this way we obtained values for the parameters of $3K/\zeta = -1.18$ and $k = 0.946$. Using the value[11] of 1050 cm⁻¹ for the one-electron spin–orbit coupling constant, ζ, for Ru³⁺, one computes a value for K of −413 cm⁻¹.

Insofar as the Ru(en)₃³⁺ complex is a representative of the much studied class of metal-tris(ethylenediamine) complexes the large negative value of the trigonal field splitting is quite interesting. For, from the single-crystal optical spectra of the Co³⁺ and Cr³⁺ complexes,[4-6] K has been estimated to be small and most probably positive (10–50 cm⁻¹), and for the Ni²⁺ complex no measurable trigonal splitting of the absorption bands was observed.[7] However, the long standing data which remain inexplicable in terms of such a small and positive valued K have been the natural circular dichroism spectra of the Co³⁺ and Cr³⁺ complexes, which would appear to require a negative K of no less than 300-cm⁻¹ magnitude.[6,8] Recent magnetic circular dichroism spectra of the Co³⁺ complex also favor a negative K of substantial magnitude.[9] Thus our epr derived value of K, if transferable to these other metal ions, supports the conclusions of the circu-
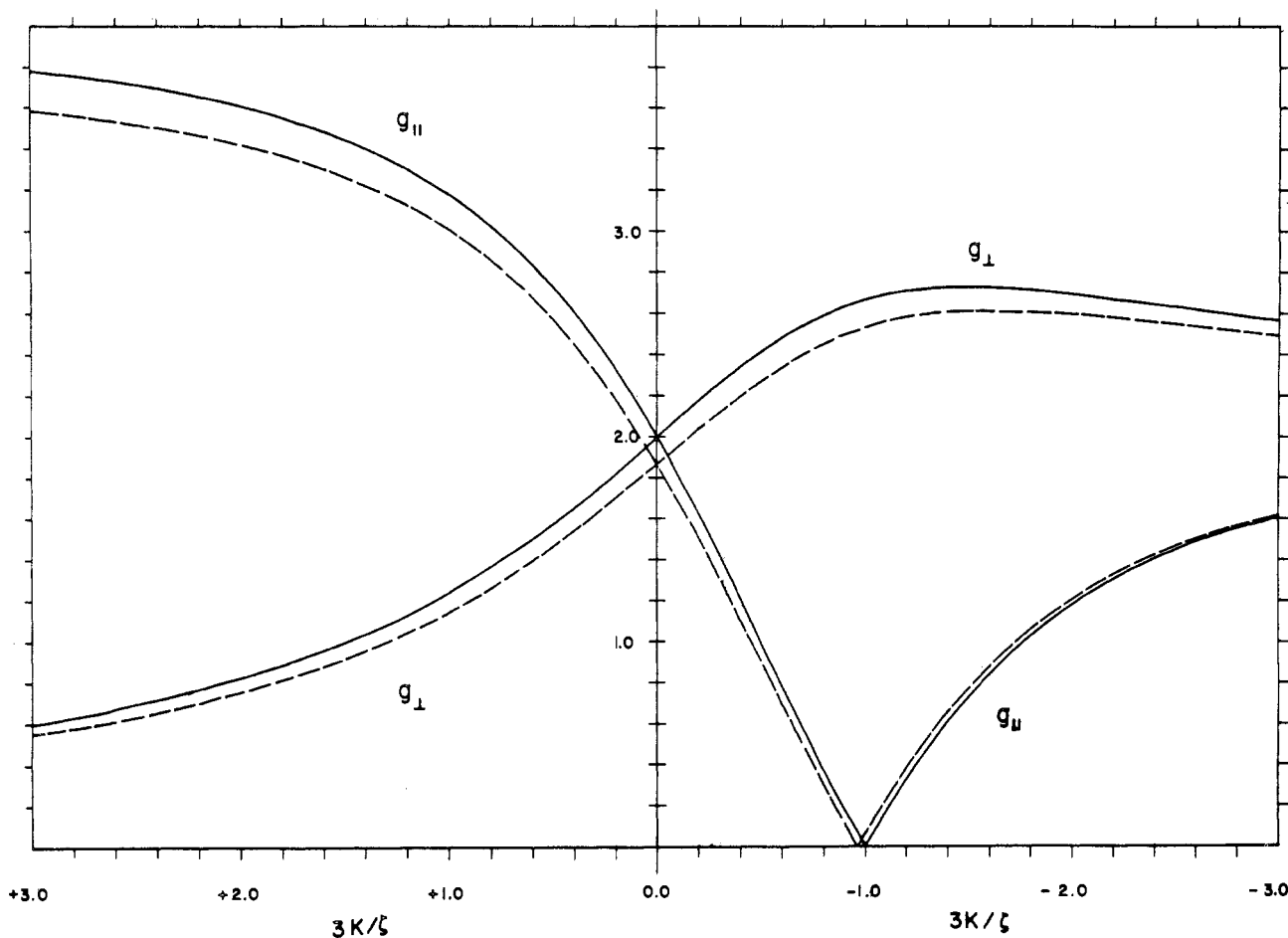
Figure 4. Plots of calculated g factors, parallel and perpendicular to the C_3 axis of the complex, for a t_{2g}^5 configuration metal ion as a function of the ratio of the trigonal field splitting of the ground state, $3K$, and the one-electron spin–orbit coupling constant, ζ. Curves are given for two representative values of the orbital reduction factor k: solid line, $k = 1.0$; dashed line, $k = 0.9$. Theoretical expressions used are given in the text.

lar dichroism studies that the effective trigonal field of three ethylenediamine ligands about a metal ion is negative (*i.e.*, K) and at least several hundred wave numbers in magnitude. In addition our results are consistent with the negative sign found for K in $Fe(en)_3^{3+}$ from magnetically perturbed Mossbauer spectra.[35] We take up below the meaning of the observed sign and magnitude of K for the ruthenium complex in terms of its known molecular structure and the current theories on the origin of the trigonal field splitting.

A simple correlation of the magnitude and sign of the trigonal field splitting parameter K with the molecular structure of a complex has long been sought. Piper and Carlin,[1] in their original analysis of this question in terms of crystal field theory, showed that the magnitude and sign of K should depend on the polar angle, σ, between the C_3 symmetry axis of the complex and the metal–ligand bond vector, and on the second- and fourth-order radial parameters $\rho_2 \sim \langle r^2 \rangle$ and $\rho_4 \sim \langle r^4 \rangle$ of the metal "d" orbital wave function. The relative magnitudes of ρ_2 and ρ_4 were originally estimated by Piper and Carlin by calculation from available metal ion radial wave functions and for all cases examined $\rho_2 > \rho_4$. For such a situation, the second-order term in the potential is dominant and the sign of K correlates with simple electrostatic considerations employing real, strong-field d orbitals; *i.e.*, for an axial compression ($\sigma > 54°\,44'$, the value of the polar angle in an octahedron) the a_1 orbital, concentrated along the trigonal axis, is stabilized, leading to the orbital

energy ordering $a_1 < e$ and a positive K; the opposite would be true for an axial elongation ($\sigma < 54°\,44'$). This fact has been reemphasized by Gerloch, *et al.*,[36] recently. However both the latter authors and Lever, *et al.*,[37] extended this crystal field treatment and showed if one departs from the theoretically predicted values of the ρ_2/ρ_4 ratio and allows it freely to assume values less than 1, an inversion of the orbital energy levels can occur and it then becomes possible to have a negative K ($e < a_1$) associated with axial compression, and a positive K ($a_1 < e$) associated with axial elongation of a complex. Table II summarizes the polar angles for a number of tris(ethylenediamine) complexes computed from the available crystal structure results. Without exception, based on the most recent and most highly refined data, these complexes all correspond to axially compressed systems with the Ru^{3+} one exhibiting the largest compression, $\sigma = 57°\,19'$, and the Co^{3+} one the least, $\sigma = 55°\,30'$. Then the negative sign found for K in the ruthenium complex, and implied for the others, can only be accounted for within the crystal field theory if the fourth-order term in the potential, $\langle r^4 \rangle$, is dominant over the second-order term $\langle r^2 \rangle$ in determining the trigonal splitting. This order of the relative magnitude of the radial parameters also appears to be the case for Ru^{3+} in other trigonal complexes from the excellent correlation of the observed sign of K with the polar angle, as shown in

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Table III. Unfortunately this pattern for the magnitudes of the radial parameters in these trigonal complexes is not readi-

Table III. Correlation of Sign of Trigonal Field Splitting Parameter, K, with the Polar Angle, σ, for Ruthenium(III)

	K^k	σ
$LuGaG^a$	+387	49° 48'
$YGaG^b$	+371	50° 36'
$LuAlG^a$	+280	51° 36'
$YAlG^b$	+273	52° 24'
$Ru(acac)_3{}^c$	+233	53° 36'^{h}
$Al_2O_3{}^d$	−250	55° 24'
$Ru(en)_3{}^{3+}{}^e$	−418	57° 19'
$Ru(ox)_3{}^{3-}{}^f$	−440	57° 30'^{i}
$Ru(phen)_3{}^{3+}{}^g$	−605	57° 45'^{j}
$Ru(bipy)_3{}^{3+}{}^g$	−670	?

^{a} Reference 15. ^{b} Reference 14. ^{c} Reference 10 and B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 422 (1966). ^{d} Reference 11. ^{e} This work and ref 20. ^{f} R. W. Olliff and A. L. Odell, *J. Chem. Soc.*, 2467 (1964). ^{g} Reference 17. ^{h} Polar angle estimate from the crystal structure of the rhodium analog, $Rh(acac)_3$: E. B. Parker, *Diss. Abstr.*, 24, 3654 (1966); J. C. Morrow, University of North Carolina, personal communication. ^{i} Polar angle estimate from the crystal structure of the rhodium analog, $Rh(ox)_3{}^{3-}$: B. Dalzell and K. Ericks, *J. Amer. Chem. Soc.*, 93, 4298 (1971). ^{j} Polar angle estimate from the crystal structure of the iron analog, $Fe(phen)_3{}^{2+}$: D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Crystallogr., Sect. A*, 21, 154 (1966). ^{k} Where only values of $3K/\zeta$ were cited, a value for ζ of 1050 cm^{-1} was used to compute K.

ly explicable but should have predictive utility in the future. It would appear, as has been suggested previously, that the ultimate origin of the trigonal splitting must be sought in the molecular orbital theory.[38-40]

In this regard Schaffer[41] has treated trigonal complexes using his angular overlap model, which is founded on the molecular orbital approach, and has predicted from it a negative K value for the $Co(en)_3{}^{3+}$ complex based only on the known angular distortions of the coordinated nitrogens from octahedral positions. Similarly, O'Reilly and Offenbacher,[42] performing a more in-depth molecular orbital calculation, were able to account successfully for the positive K values observed for the Ru^{3+} ion in the axially elongated RuO_6 units in garnets.

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Reduction of Oxygen by Hexaammineruthenium(II) and by Tris(ethylenediamine)ruthenium(II)

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The reaction of $Ru(NH_3)_6{}^{2+}$ with oxygen takes place quantitatively according to the stoichiometry: $2Ru(NH_3)_6{}^{2+} + 2H^+ + O_2 = 2Ru(NH_3)_6{}^{3+} + H_2O_2$. The rate law over a wide range of Ru(II), O_2, and H^+ concentrations (1.00 M H^+ to pH 6.05) has the form $-d[O_2]/dt = k[Ru(II)][O_2]$. At 25° and $\mu = 1.00$ maintained with LiOAc, $k = 1.26 \times 10^2$ M^{-1} sec^{-1}. With $Ru(en)_3{}^{2+}$ as the reducing agent, the first stage involving oxidation to $Ru(en)_3{}^{3+}$ takes place rapidly enough so that this stage can be studied with initially no complication caused by oxidation of the ligand. If published values of $E°$ for the Ru(III)–Ru(II) and O_2–$O_2{}^-$ couples are correct, we conclude that the reaction does not involve $O_2{}^-$ as an intermediate. The oxidation of $Ru(NH_3)_6{}^{2+}$ by H_2O_2 is a very slow reaction, and under the optimum conditions we were able to realize, we were dealing not with the intrinsic reaction but with a path involving catalysis by iron salts. The specific rate for the oxidation of $Ru(NH_3)_6{}^{2+}$ by O_2 is at least 10^4 times greater than for the oxidation by H_2O_2.

A particular point of interest in the reactions with oxygen to be described is that the metal ion reducing agents retain their primary coordination spheres intact. To our knowledge, no other system of this type has been subjected to a detailed kinetic analysis. A second point of interest is that the reduction of O_2 to H_2O_2 is much more facile than that of H_2O_2 to H_2O. In this respect, the system is by no means unique, H_2O_2 having been identified as an intermediate stage in the reduction of O_2 by Eu(II)[1] and Pu(III).[2] However, with Eu(II) and Pu(III) as reducing agents there is no ready means of establishing whether, when oxygen acts upon them, the oxidant makes use of a normal coordination position on the metal. For our system, it can be concluded with certainty

that O_2 does not occupy a normal coordination position in oxidizing $Ru(NH_3)_6{}^{2+}$, and this places an important limitation on the mechanisms which are possible for the reaction. Another point of interest has been emphasized by recent work[3-5] on the reaction of molecular oxygen with tris(ethylenediamine), hexakis(methylamine), and other substituted amine complexes of ruthenium(II) which describe evidence for oxidation of the ligands. We have established the first step in the reaction of molecular oxygen with tris(ethylenediamine)ruthenium(II) as being oxidation to tris(ethylenediamine)ruthenium(III). By continued action of oxygen or of other oxidizing agents tris(ethylenediamine)-

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