EPR Spectra of an Exchange-Coupled Gd(III)–Ru(III) Pair: A Novel Heterogeneous Magnetic Dimer

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Abstract: The EPR spectra of $CsMgCl_3$ crystals doped with Gd(III) and Ru(III) contain the resonances from a magnetically coupled Gd(III)–Ru(III) pair. The pair spectrum exhibits the fine structure characteristic of a Gd(III) ion ($S = {}^7/_2$) in an axial lattice site. At 77 K the weak coupling with the Ru(III) ion ($S = {}^1/_2$) splits each resonance into a doublet. The spectrum is well enough resolved to allow a characterization as a function of crystal orientation. A spin Hamiltonian which assumes a simple anisotropic interaction between the two ions is adequate to describe the spectrum ($\mathcal{H}_p = J_z\hat{S}_z\hat{S}_z' + J_{xy}(\hat{S}_y\hat{S}_x' + \hat{S}_y\hat{S}_y')$; where $|J_z| = +0.0055$ cm^{-1} and $|J_{xy}| = 0.020$ cm^{-1}). The analysis determines that the principal g values of Gd(III) and Ru(III) have opposite signs (for Gd(III): $g_z = +1.991$ and $|g_{xy}| = 1.991$; for Ru(III): $g_z' = -2.35$ and $|g_{xy}'| = 1.62$). The magnetic properties of the Gd(III)–Ru(III) dimer are discussed. As a part of this analysis, the spectra of a number of monomeric centers containing Gd(III) and Ru(III) were characterized. The properties of these centers are also discussed.

The linear chain $CsMX_3$ salts such as $CsMgCl_3$ will incorporate low concentrations of a variety of trivalent metals into the crystal lattice as substitutional impurities.[1-9] The trivalent impurities replace the divalent ions of the host lattice in a manner which maintains the local charge balance. As a result the trivalent ions tend to aggregate in pairs in association with a divalent ion vacancy to give a linear M(III)–vacancy–M(III) system (designated as M(III)–M(III)) which is electrostatically equivalent to the three displaced divalent ions. When more than one kind of trivalent ion is present, heterogeneous as well as homogeneous pairs are formed.[2,4,5] The presence of small monovalent ions such as lithium or sodium provides an alternate means by which trivalent ions may eneter the linear chain $CsMX_3$ lattice.[2,4,8] A small monovalent ion and a trivalent ion occupy adjacent divalent ion sites to give a M(III)–M′(I) center which is the charge equivalent of the two displaced divalent ions. It is the unique feature of the linear chain $CsMX_3$ salts that a wide variety of metal ions can be brought together in dimeric centers which are well defined and occur in high relative abundance. The crystal lattice has high symmetry and is ideal for spectroscopic studies. In both M(III)–M′(III) and M(III)–M′(I) centers, the two impurity ions are close enough for significant interactions. Since the incorporation of trivalent impurities is largely determined by electrostatics, M(III)–M′(III) and M(III)–M′(I) centers can be prepared with a wide range of metal ions. Dimeric centers containing unusual combinations of metal ions are produced in concentrations which allow straightforward spectroscopic characterization.

As a part of a systematic study of these impurity centers, the EPR spectrum of $CsMgCl_3$ crystals doped with trivalent gadolinium and ruthenium has been investigated and shows the presence of Gd(III)–Ru(III) centers. At 77 K the spectrum is sufficiently resolved that a detailed analysis is possible. A magnetic dimer containing Gd(III) and Ru(III) is particularly interesting, since it is a system with coupled d and f electrons. It is standard practice to describe a magnetically coupled pair of ions by a spin Hamiltonian of the form shown below.[10-12]

$$\mathcal{H} = \mathcal{H}_p + \mathcal{H}_s + \mathcal{H}_s'$$

The terms describing the interaction between the two paramagnetic ions are contained in $\mathcal{H}_p$ while the single-ion terms appear in $\mathcal{H}_s$ and $\mathcal{H}_s'$. The EPR spectra of centers with Gd(III) and Ru(III) paired with a number of diamagnetic ions werre investigated to obtain reasonably estimates of the single-ion parameters in $\mathcal{H}_s$ and $\mathcal{H}_s'$. This paper describes the analysis of the spectrum from the Gd(III)–RuIII) dimer and the properties of the other Gd(III)- and Ru(III)-containing centers.

Experimental Section

The host material, $CsMgCl_3$, was prepared by fusing equimolar mixtures of CsCl and anhydrous $MgCl_2$ under vacuum. Except for Gd(III), the metal ion impurities (Ru(III), In(III), Ir(III), La(III), Li(I), Na(I), and Cu(I)) were introduced by adding small amounts of the appropriate metal chlorides to samples of $CsMgCl_3$ and fusing the resulting mixtures in evacuated vycor ampules. Anhydrous GdI_3 was used to prepare the Gd(III)-containing materials. The $CsMgCl_3$ samples with small quantities of GdI_3 were fused under vacuum and then exposed to a partial pressure of Cl_2 to displace the iodide ions. Crystals were grown by the Bridgman method. The apparatus has already been described.[13] Because of the hygroscopic nature of $CsMgCl_3$, the manipulations were performed in a nitrogen-filled glovebox. The presence of Ru(III) imparts a noticeable red-brown coloration to the doped crystals.

EPR Spectra. Small crystals suitable for EPR spectroscopy were cleaved from the crystalline boules obtained by the Bridgman procedure. The tendancy of $CsMgCl_3$ to cleave along the crystallographic c axis is very helpful in mounting and orienting the samples. The doped crystals were covered with "Duco" cement and mounted on quartz rods in a manner which would allow the EPR spectra to be studied as a function of the angle between the applied field and the c axis (θ). This requires the c axis to be contained in the rotation plane of the magnetic field. Spectra were recorded at room and liquid-nitrogen temperature on a Varian E-3 X-band spectrometer with 100-KHz modulation.

Results and Discussion

EPR Spectra and Analysis. Like a number of other $CsMX_3$ salts, $CsMgCl_3$ adopts a hexagonal perovskite structure in which the MX_6^{4-} octahedra share opposite faces to form infinite linear chains.[14,15] The cesium ions occupy positions between the $[MX_3^-]_n$

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Table I. Single-Ion Parameters of Gd(III)–M′ and Ru(III)–M′ Centers in $CsMgCl_3$

Gd(III)–M′ Centers (Room Temperature)

	Gd(III)–Li(I)	Gd(III)–Na(I)	Gd(III)–In(III)	Gd(III)–La(III)	Gd(III)–Gd(III)[a]
g_z	1.991	1.991	1.991	1.991	1.991
g_{xy}	1.991	1.991	1.991	1.991	1.991
b_2^0, cm^{-1}	±0.0330	±0.0443	±0.0447	±0.0429	+0.0450
b_4^0, cm^{-1}	±0.0006	±0.0005	±0.0009	±0.0009	+0.0010
b_6^0, cm^{-1}	±0.0001	±0.0001	±0.0001	±0.0001	+0.0001

Ru(III)–M′ centers (77 K)[b]

	Ru(III)–Li(I)	Ru(III)–Na(I)	Ru(III)–Cu(I)	Ru(III)–In(III)	Ru(III)–Ir(III)
g_z'	2.93	2.95	2.58	2.37	2.33
g_{xy}'	1.24	1.22	1.47	1.61	1.62
g_{av}'	1.80	1.80	1.84	1.86	1.86

[a] Taken from ref 3. [b] The signs of the g values are not determined in the experiment.

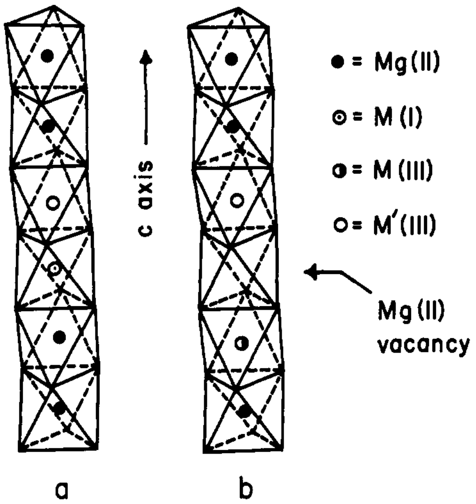

Figure 1. Perspective views of the $[MgCl_3^-]_n$ chains showing the M(III)–M′(I) center (a) and the M(III)–M′(III) center (b). The corners of the octahedra are occupied by chloride ions.

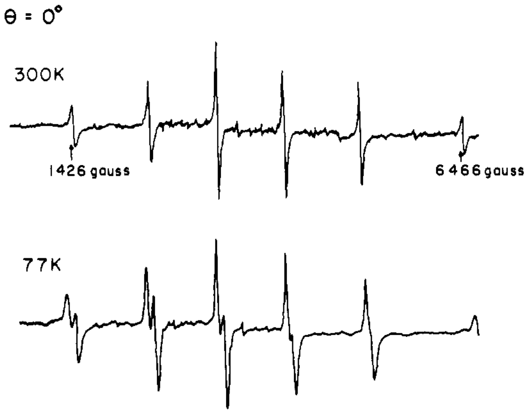

Figure 2. EPR spectrum of a $CsMgCl_3$ crystal doped with Gd(III) and Ru(III) recorded at room and liquid-nitrogen temperature with the magnetic field directed along the crystallographic c axis ($\theta = 0°$). One of the seven fine structure components expected for an $S = {}^7/_2$ system falls outside the range of the spectrometer ($H < 600$ G).

chains and balance the anionic charge. Although the incorporation of impurity ions must cause some local lattice distortions, the basic geometry of the M(III)–M′(III) and M(III)–M′(I) impurity centers is determined by the linear chain structure of the host material (see Figure 1). If $CsMgCl_3$ is viewed as a rigid spectroscopically inert matrix, a M(III)-M′(III) center consists of two independent octahedral MCl_6^{3-} complexes which approach each other along a common threefold axis. The M(III)-M′(I) center can be described as a dimer formed from two octahedral complexes joined at a common face. Both types of centers have C_{3v} symmetry with the threefold axis passing through the two impurity ions. This threefold axis corresponds to the crystallographic c axis of the $CsMgCl_3$ crystal. Approximate molecular geometries for the centers can be extracted from the known structural properties of the host material. In $CsMgCl_3$ the distance between adjacent divalent ion sites within the linear chain is 3.09 Å and the Mg–Cl–Mg angle is 76.6°.[15]

The EPR spectra of $CsMgCl_3$ crystals doped with Gd(III) and Ru(III) contain a series of relatively intense resonances which obviously arise from the Gd(III)–Ru(III) center. As shown in Figure 2, the room temperature spectrum exhibits a fine structure pattern characteristic of a magnetically isolated Gd(III) ion ($S = {}^7/_2$). One component of the seven-line fine structure, the low-field $|\pm{}^5/_2\rangle \leftrightarrow |\pm{}^7/_2\rangle$ transition, falls below the minimum field of the spectrometer (600 G) when the magnetic field is parallel to the crystallographic c axis. All seven lines are seen when the field is perpendicular to the c axis. At 77 K, the resonances split into doublets. This splitting cannot be attributed to a simple lattice effect such as the existence of two structurally distinct crystal sites for the Gd(III)–Ru(III) centers. It is clear from the angular dependence that the spectrum is not the superposition of resonances from two types of Gd(III) ions which have slightly different zero-field parameters. We conclude that the splitting of the Gd(III) resonances arises from the magnetic interactions with the spin of the Ru(III) ion ($S = {}^1/_2$). Apparently the spin relaxation of the Ru(III) ion is sufficiently fast at room temperature that the interaction with Gd(III) ion are effectively averaged out. These observations indicate that the coupling between the two ions is rather weak. Weak coupling would be expected since a M(III)–M(III) center contains no direct superexchange pathways. The single-ion parameters of a paramagnetic ion in a crystal are largely determined by the immediate surroundings. The environment of a given trivalent ion in a M(III)–M′(III) center should be nearly independent of the nature of the second trivalent ion. Reliable estimates of the single-ion parameters may be taken directly from the spectra of M(III)–M′(III) centers where the second trivalent ion is diamagnetic.[2,4]

Crystals of $CsMgCl_3$ containing a variety of centers with Gd(III) and Ru(III) paired with diamagnetic ions were grown and studied. Although the M(III)–M′(III) centers are of primary importance, a number of M(III)–M′(I) centers were also characterized. Consistent with earlier work, the spectra of the Gd(III) centers are described by the following axial spin Hamiltonian.[2]

$$\mathcal{H}_s = g_z\mu_B H_z\hat{S}_z + g_{xy}\mu_\beta(H_x\hat{S}_x + H_y\hat{S}_y) + (b_2^0/3)O_2^0 + (b_4^0/60)O_4^0 + (b_6^0/1260)O_6^0$$

The first two terms describe the electron Zeeman interaction while the last three terms define the zero-field splitting. The O_n^0 operators are defined according to standard notation.[16] The parameters obtained from the spectra of various centers are given

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Table II. Electronic Structure of the Ru(III) Ion in the Ru(III)–M′ Centers in $CsMgCl_3$

center	k	α, deg	ν/ξ
Ru(III)–Li(I)	0.91	23.0	−0.87
Ru(III)–Na(I)	0.91	22.7	−0.89
Ru(III)–Cu(I)	0.91	27.4	−0.50
Ru(III)–In(III)	0.91	29.9	−0.32
Ru(III)–Ir(III)	0.90	30.3	−0.30
Ru(III) in YAG[a]	0.92	23.9	−0.78
Ru(III) in YGG[a]	0.94	21.1	−1.06

[a] Taken from ref 24.

in Table I. The g values are isotropic within experimental error. As expected the parameters of all of the Gd(III)–M(III) centers are quite similar. The absolute signs of the zero-field parameters are not determined by the spectra of the Gd(III)–M(III) centers; however, the analysis of the magnetically coupled Gd(III)–Gd(III) center defines the parameters to be positive.[3] It seems certain that the signs are the same in the other Gd(III) centers.

The crystals of $CsMgCl_3$ doped only with Ru(III), which presumably contain Ru(III)–Ru(III) centers, exhibit no detectable EPR resonance at room or liquid-nitrogen temperature. The explanation for this observation is not clear. It seems unlikely that the exchange interactions are strong enough to completely quench the paramagnetism at these temperatures. Crystals containing Ru(III) dodoped with various diamagnetic ions do give observable EPR resonances at 77 K. These resonances are fairly broad but can be followed as a function of crystal orientation. The Ru(III) ion is a low-spin d^5 system with a single unpaired electron which is described by a rather simple spin Hamiltonian.

$$\mathcal{H}_x' = g_z'\mu_B H_z \hat{S}_z' + g_{xy}'\mu_B(H_x\hat{S}_x' + H_y\hat{S}_y')$$

We have adopted the convention that the primed spin operators refer to the Ru(III) ion while the unprimed operators refer to the Gd(III) ion. The experimentally determined g values for the various Ru(III) systems are given in Table I. There is a noticeable difference between the Ru(III)–M(III) centers and the Ru(III)–M(I) systems. The Ru(III)–In(III) and Ru(III)–Ir(III) centers undoubtedly provide the best indication of the properties of the ruthenium ion in the Gd(III)–Ru(III) center.

Orbital angular momentum is not quenched in a t_2^5 configuration. As a result the g values of Ru(III) may take on positive and negative values.[17-23] The numbers given in Table I represent absolute values, since the signs cannot be directly determined from the EPR spectra. The magnitudes of the g values do, however, provide insight into the electronic structure of the Ru(III) ion. Neglecting configuration interaction, the wave functions of the ground-state doublet of a t_2^5 ion in a trigonal environment are shown below.[24]

$$|+) = (\sin\alpha)|O^+) + (\cos\alpha)[{}^2\!/_3|{-2^-}) + {}^1\!/_3|{+1^-})]$$

$$|-) = (\sin\alpha)|O^-) + (\cos\alpha)[{}^2\!/_3|{+2^+}) + {}^1\!/_3|{-1^+}\rangle]$$

The g values are then given by the following equation.[25]

$$g_z = 2|(1 + k)\cos^2\alpha - \sin^2\alpha|$$

$$g_{xy} = 2|k(2^{1/2})\cos\alpha\sin\alpha + \sin^2\alpha|$$

The parameter k is the orbital reduction factor ($k = \langle\phi|\hat{L}_z|\phi\rangle/\langle d|\hat{L}_x|d\rangle$) which allows for metal-to-ligand delocalization. From the observed g_z and g_{xy} values it is possible to compute k and α.

Table III. Spin Hamiltonian Parameters for the Gd(III)–Ru(III) Center in $CsMgCl_3$

single-ion parameters		interaction parameters	
g_z	1.991	J_z, cm^{-1}	+0.0055
g_{xy}	1.991	J_{xy}, cm^{-1}	±0.020
b_2^0, cm^{-1}	+0.0476		
b_4^0, cm^{-1}	+0.0010		
b_6^0, cm^{-1}	+0.0001		
g_z'	−2.33		
g_{xy}'	±1.62		

The α value can be related to the ratio between the trigonal splitting (ν) and the spin orbital coupling constant (ξ).

$$\tan 2\alpha = \frac{2^{1/2}}{(1/2 - \nu/\xi)}$$

Table II presents the calculated values of ν, k, and ν/ξ for the centers in $CsMgCl_3$. The data for Ru(III) in yttrium aluminum garnet (YAG) and yttrium gallium garnet (YGG) are included for comparison. The electronic properties of the centers in $CsMgCl_3$, the Ru(III)–Li(I) and Ru(III)–Na(I) systems in particular, are strikingly similar to those of the Ru(III) ion in the garnet crystals. The k values indicate a small amount of metal-to-ligand delocalization (less than 10%). The structural data for YAG, YGG, and $CsMgCl_3$ indicate that the metal ion sites deviate from regular octahedral geometry as a result of trigonal elongations.[15,24] The degree of distortion is indicated by the value of σ, the angle between the trigonal axis and one of the metal–ligand bonds. In a regular octahedron, the σ angle is 54.75°. The trigonal distortions are comparable in all three lattices, as evidenced by σ angles of 52.4°, 50.6°, and 51.7° for YAG, YGG, and $CsMgCl_3$, respectively. The ν/ξ ratios for all of the centers have the same sign; however, the magnitudes vary somewhat. The magnitudes of ν/ξ for the Ru(III)–In(III) and Ru(III)–Ir(III) centers are noticeably smaller than those of the other centers. This may simply reflect the fact that there are significant local lattice distortions associated with a M(III)–M′(III) center.

Now that the single-ion parameters have been reasonably well established, it is possible to analyze the spectrum of the magnetically coupled dimer. The interaction Hamiltonian shown below is probably the simplest expression that could realistically be expected to describe the Gd(III)–Ru(III) center.

$$\mathcal{H}_p = J_z\hat{S}_z\hat{S}_z' + J_{xy}(\hat{S}_x\hat{S}_x' + \hat{S}_y\hat{S}_y')$$

This Hamiltonian assumes an anisotropic interaction. The total dimer Hamiltonian is the sum of the three parts, $\mathcal{H}_p + \mathcal{H}_s + \mathcal{H}_s'$, for which the product functions, $|S,m\rangle|S',m'\rangle$, serve as the basis set. For a dimer containins an $S = {}^7\!/_2$ ion coupled to an $S = {}^1\!/_2$ ion, there will be 16 product functions. In this study, the 16 × 16 Hamiltonian matrix was solved numerically by a computer-diagonalization procedure which computes the resonance fields by iteration. The parameters were varied until good agreement between the observed and calculated resonance fields was obtained. Presuming that the Gd(III) ion g values are positive, it is necessary to assign a negative value to g_z' and a positive value of J_z to produce a reasonable fit. (See the discussion in the following section.) Equally good fits result when J_{xy} and g_{xy}' are both taken to be positive or both taken to be negative. The final parameters for the Gd(III)–Ru(III) center are given in Table III. These parameters give a good overall description of the angular dependence of the EPR spectrum (see Figure 3). The fit is as good as could be expected in view of the relatively large line widths (~100 G peak to peak) which limit the precision of the observed resonance fields.

The weak coupling scheme which we have adopted to treat the Gd(III)–Ru(III) dimer predicts that the Ru(III) resonance will be split into eight components by the ${}^7\!/_2$ spin of the Gd(III) ion. It is disappointing that there are no features in the observed spectrum which can be assigned to the Ru(III) ion. In part, this may simply reflect the fact that the Ru(III) resonance is much less intense than the Gd(III) resonance. If the resonances from

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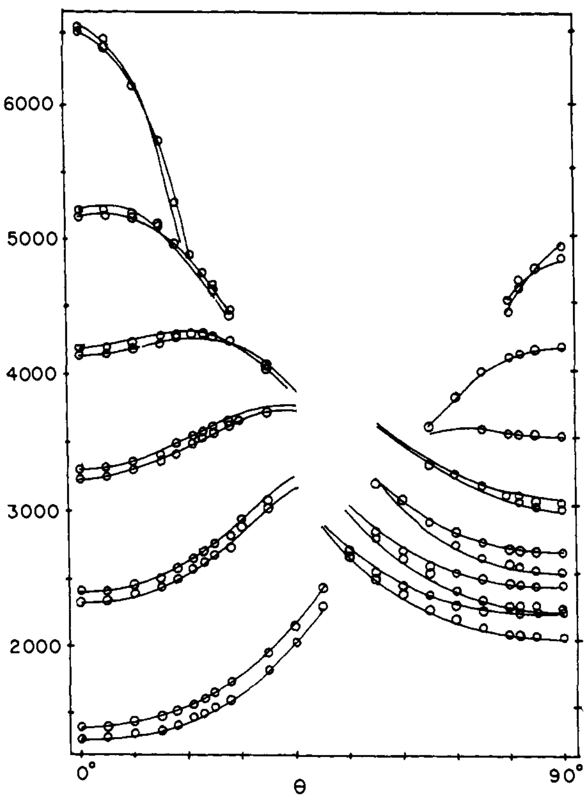

Figure 3. Angular dependence of the EPR spectrum of the Gd(III)-Ru(III) center. The resonance fields are plotted on the vertical axis while the angle between the field and the crystallographic *c* axis, θ, is shown on the horizontal axis. The open circles represent the observed resonance fields. The solid lines were calculated with the spin Hamiltonian parameters given in Table III.

the Gd(III)-Ru(III) dimer obey the normal EPR selection rules, the intensity of a resonance is proportional to the square of the transition moment as shown below.

$$I \propto |\langle S,m|\hat{S}_+ + \hat{S}_-|S,m\rangle|^2$$

This expression gives relative intensities of 7:12:15:16:15:12:7 for the seven allowed ($\Delta M = \pm 1$) transitions of a sytem with a spin of $^7/_2$. By the same expression the relative intensity of the resonance from a system with a spin of $^1/_2$ is 1. This disparity is compounded by the fact that the Ru(III) resonance is split into eight components while the Gd(III) resonances are only split into two components. Thus, each component of the Ru(III) resonance will be weaker than the least intense of the Gd(III) resonances by a factor of 28. At this low level of intensity, lines from other paramagnetic centers in the $CsMgCl_3$ crystals cover much of the spectrum. Although the failure to observe the Ru(III) resonance does add an element of doubt, the angular dependence of the Gd(III) resonances is sufficiently unique and the agreement between theory and experiment is good enough that we feel our analysis must be basically correct.

Magnetic Properties of the Gd(III)-Ru(III) Dimer. Although the Gd(III)-Ru(III) dimer is novel in a number of respects, the *g* values are probably the most interesting feature of this magnetically coupled system. In a paramagnetic system only the sign of the product of the three principal *g* values ($g_xg_yg_z$) has physical significance.[20,26] If the system has axial symmetry, the unique *g* value, g_z, determines the sign of the product. The analysis unambiguously establishes that g_z and g_z' have opposite signs in the Gd(III)-Ru(III) dimer. An ion such as Gd(III) with a $4f^7$ configuration should approach spin-only behavior since the orbital angular momentum is nearly quenched in a half-filled shell. It seems certain that g_z is positive which then requires g_z' to be negative. The Gd(III)-Ru(III) system is an unusual case where the absolute sign of the $g_xg_yg_z$ product of a t_2^5 ion is established by a simple magnetic resonance experiment. The g_z' values for the other Ru(III)-M systems are probably also negative since the immediate environments (first coordination spheres) of the Ru(III) ion are similar in all of the impurity centers in $CsMgCl_3$.

Table IV. Analysis of the Magnetic Coupling in the Gd(III)-Ru(III) Center

	g_{xy}' and J_{xy}	
parameter	positive	negative
J, cm^{-1}	-0.0125	+0.0248
D, cm^{-1}	+0.0085	-0.0048
D_d, cm^{-1}	+0.0084	+0.0044
J_d, cm^{-1}	+0.0019	+0.0105
J_e, cm^{-1} [a]	-0.0144	+0.0143

[a] Calculated assuming $J = J_e + J_d$.

It is important to point out that the EPR spectrum which arises from a heterogeneous magnetic dimer is strongly influenced by the ratio $|J/\Delta g\beta H|$ (where $g\Delta = g - g'$).[11] If exchange interactions are large relative to the Δg term, the dimer will be strongly coupled and the EPR spectrum will exhibit the features characteristic of the dimer as a whole. A spin of $^7/_2$ coupled to a spin of $^1/_2$ gives a two-state manifold, one with a total spin of 3 and the other with a total spin of 4. If both states are thermally populated, the fine structures associated with spins of 3 (6 lines) and 4 (8 lines) should appear in the EPR spectrum. When $J/\Delta g\beta H$ is small, the dimer will be uncoupled and the EPR spectrum will contain the features characteristic of each individual ion. This is clearly the case with the Gd(III)-Ru(III) dimer where the spectrum shows the fine structure of an $S = {}^7/_2$ ion which is only weakly perturbed by a spin of $^1/_2$. The fact that the magnitude of the Δg term is large compared to the exchange interactions is a direct consequence of the *g* values of Gd(III) and Ru(III) being of opposite signs.

The magnetic interactions between Gd(III) and Ru(III) can be analyzed theoretically. The interactions can be partitioned into an isotropic component (J) and an anisotropic component (D).

$$J_z = J + 2D \qquad J_{xy} = J - D$$

Since the spectral analysis does not define the sign of J_{xy}, two sets of J and D parameters must be considered (see Table IV).

The through-space or dipolar coupling of the two paramagnetic ions (D_d) will contribute to the anisotropic component of the interaction. The following equation is a point dipole expression[11] which we have modified to treat a heterogeneous dimer.

$$D_d = -(\mu_B{}^2/3R^3)(2g_zg_z' + g_{xy}g_{xy}')$$

The R corresponds to the distance between the two dipoles. In general, the interaction due to electron exchange (J_e) will account for the isotropic coupling (J); however, the Ru(III) ion has an anisotropic *g* tensor so that the dipolar coupling will also contribute (J_d). The value for J_d can be computed from the modified point dipole expressions shown below.

$$J_d = (\mu_B{}^2/3R^3)(2g_Xx_yg_{xy}' - 2g_zg_z')$$

The total isotropic interaction is simply the sum of the exchange and dipolar contributions. Assuming an interionic separation of approximately 6 Å (twice the Mg-Mg distance), the dipolar terms can be calculated by using the *g* values that are determined by the spectral analysis. The component of the isotropic interaction which results from electron exchange can then be determined by difference. The results of these computations are presented in Table IV. When the g_{xy}' and J_{xy} are taken to be positive, the calculated value for D_d is in very good agreement with the observed anisotropic interaction, D. When the negative sign combination is used, the value of D_d has the correct magnitude but the wrong sign. The calculation with J_{xy} and g_{xy}' positive clearly gives better results, if the anisotropic coupling is dipolar in origin. Unfortunately, effects such as pseudo-dipolar exchange with are difficult to accurately compute may also contribute to the anisotropic interaction.[11] Thus, an absolutely certain sign assignment cannot be made from the available data. The two sign combinations lead

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to electron-exchange interactions (J_e) of the same absolute value ($\sim$0.014 cm^{-1}) but opposite in sign. The magnitude of J_e for the Gd(III)–Ru(III) dimer is more than ten times greater than that for the homogeneous Gd(III)–Gd(III) dimer.[3] (For the Gd(III)–Gd(III) center in $CsMgCl_3$, J_e is about 0.0011 cm^{-1}.) This result is consistent with the view that the d electrons of the transition-metal ions are considerably more delocalized than the f electrons of the rare-earth ions. The strength of the exchange coupling in the homogeneous Ru(III)–Ru(III) dimer is not known; however, the interactions in other d-electron systems such as the Cr(III)–Cr(III), Cr(III)–Mo(III), and Mo(III)–Mo(III) centers fall in the 1 to 3 cm^{-1} range.[5,7]

In summary, the Gd(III)–Ru(III) center in $CsMgCl_3$ has been shown to be a weakly coupled magnetic dimer where the g values of the two ions have opposite signs. The electron-exchange interactions are in the order of 0.014 cm^{-1}, but it is not clear if the coupling is ferromagnetic or antiferromagnetic.

Registry No. Gd(III), 22541-19-1; Ru(III), 22541-88-4; $CsMgCl_3$, 13845-09-5.

Models of the Cytochromes *b*. 5. EPR Studies of Low-Spin Iron(III) Tetraphenylporphyrins

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Abstract: The EPR spectra of a wide range of tetraphenylporphyrin complexes of Fe(III) have been investigated as a function of solvent, ligand type, ligand basicity, porphyrin substituents, covalent attachment of axial ligands, and mixed axial ligand coordination. The results show the following: (1) EPR parameters of low-spin bis-axial ligand complexes of Fe(III) porphyrins depend not only on ligand basicity but also on ligand type. Of the three major classes studied, bis(imidazole) and -(aminopyridine) complexes all have similar values of g_x, g_y, and g_z which are nearly independent of ligand basicity, while bis(pyrazole) (and bis(indazole)) complexes have g_x, g_y, and g_z values which tend to converge as ligand basicity increases. (2) The effect of the electron-donating or -withdrawing nature of phenyl substituents on the EPR parameters of a large series of phenyl-substituted (TPP)Fe(N-MeIm)$_2^+$ derivatives is very small: The rhombicity $V/\Delta = 0.64 \pm 0.01$ for all complexes, while the tetragonality Δ/λ ranges from 2.97 for electron-donating substituents to 3.33 for electron-withdrawing substituents, the opposite trend from that expected for increasing axial ligand donor strength. No difference was observed in the EPR parameters of unsymmetrically as compared to symmetrically substituted TPP derivatives. (3) Covalent attachment of axial ligands or steric crowding of externally supplied axial ligands in the hope of seeing variation in the EPR parameters with relative axial ligand plane orientation (parallel vs. perpendicular) was not successful in producing pure isomers, and thus no effects on EPR parameters with axial ligand plane orientation were detected. (4) A covalently attached (N-alkylimidazole–TPP)Fe(III) derivative was utilized to allow formation of mixed-ligand low-spin Fe(III) complexes. The alkylimidazole–imidazolate ligand combination was only very slightly more tetragonal than its protonated imidazole counterpart, while the alkylimidazole–pyrazole, 3-aminopyrazole, 1,2,4-triazole, and 2-methylimidazole mixed ligand complexes all had EPR parameters uniquely different from those of the parent bis-ligand complexes. Discussion of these results in light of the g values of membrane-bound cytochromes b, c, and a_3 bound to cyanide is also included.

EPR spectroscopy has for many years been one of the most useful tools for characterizing ferric hemoproteins[2-52] and model hemins.[14,53-67] Of the three EPR-active spin states ($S = {}^5/_2$, ${}^3/_2$, and ${}^1/_2$), the low-spin ferriheme proteins have been studied in most

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