We are currently examining two aspects of these new photoredox reactions: the barrier toward regeneration of $V(NN)_3^{2+}$ from the vanadium(III) solutions[35] and the photochemical properties of vanadium(II) complexes of strong field ligands such as isocyanides[36] and phosphines.[37] In these complexes both MLCT and d–d quartet excited states should be well above ^2E, so that their excited-state lifetimes should be significantly longer than those observed here.

Another area we are now exploring is the capacity of $V_2(NN)_4(\mu\text{-OH})_2^{4+}$ for additional electron transfer. Bennett and Taube observed disproportionation following one-electron thermal oxidation of $V(2,2'\!:\!6',2''\text{-terpyridine})_2^{2+}$;[10] thus, we are studying both disproportionation (reaction 8) and thermal electron transfer to A (reaction 9) as second steps in photoinitiated overall two-

$$V_2(NN)_4(\mu\text{-OH})_2^{4+} + NN \rightarrow VO(NN)_2^{2+} + V(NN)_3^{2+} + H_2O \tag{8}$$

$$V_2(NN)_4(\mu\text{-OH})_2^{4+} + 2A \rightarrow 2VO(NN)_2^{2+} + 2A^- + 2H^+ \tag{9}$$

electron-transfer schemes based on these vanadium complexes.

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Exact Results for EPR g and A Tensors in the $S_1 = 1, {}^3/_2, 2, {}^5/_2$ and $S_2 = {}^1/_2$ Spin-Coupled Systems. The Effect When S Is Not a Good Quantum Number

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Exact expressions for the EPR **g** and **A** tensors in spin-coupled systems are given in terms of the parameters from the isolated spins for $S_1 = 1, {}^3/_2, 2, {}^5/_2$ and $S_2 = {}^1/_2$. These results include the effect of interactions between different spin manifolds, i.e. when S is not a good quantum number. The **g** tensor and the hyperfine tensors are rather sensitive measures of the intermanifold coupling, thus making EPR an excellent probe of spin-coupling parameters. The resonance positions for selected spin states are given in terms of observed g values. In the presence of significant intermanifold interaction the observed g values along the major axes do not simply correspond to the principal components of the molecular **g** tensor.

Introduction

The study of binuclear spin-coupled systems has been of longstanding interest.[1] Primary interest has been in homobinuclear systems where $S_1 = S_2$, the classic example being the work of Bleaney and Bowers on the copper acetate dimer.[2] However, heterobinuclear systems have been increasingly studied both because the magnetic properties for $S_1 \neq S_2$ systems are of fundamental interest[3-8] and because a number of biological systems have different spin-coupled metal ions associated with the active site.[9-13]

Electron paramagnetic resonance (EPR) spectroscopy has been an important tool for elucidating the properties of spin-coupled systems.[3,4,14-16] This technique conveniently probes the ground state and, in favorable cases, the first excited spin manifold. The data derived from the EPR spectrum are the **g** tensor and, if one (or both) of the nuclei have spin, the hyperfine coupling tensor(s), **A**. The interaction between the spins can substantially alter the magnitude of the components of the **g** and **A** tensors relative to the single-spin values, and the relationship between the parameters in the coupled state and the parameters of the single uncoupled spins is of fundamental interest.[17] This relationship has been studied in the past, but the equations presented always include the assumption that coupling between various spin manifolds is negligible, i.e., the total spin S has been assumed to be a good quantum number. The existence of matrix elements that connect different spin states has been recognized,[7,12,17,19] but the explicit

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Table I. Results for $S_1 = 1$, $S_2 = {}^1/_2{}^a$

state	energy	$\mathbf{A}_1{}^c$	$\mathbf{A}_2{}^c$	$\mathbf{g}^c$
$\vert {}^3/_2\ \pm{}^3/_2\rangle$	$(1/2)D(\lambda + 2)$	$(2/3)\mathbf{A}_1$	$(1/3)\mathbf{A}_2$	$(2/3)\mathbf{g}_1 + (1/3)\mathbf{g}_2$
$(\cos\theta)\vert {}^3/_2\ \pm{}^1/_2\rangle \pm (\sin\theta)\vert {}^1/_2\ \pm{}^1/_2\rangle$	$(1/2)D(\lambda - 2 + 2(2^{1/2})\tan\theta)$	$(1 - (1/3)f_1(\theta))\mathbf{A}_1$	$(1/3)f_1(\theta)\ \mathbf{A}_2$	$(1 - (1/3)f_1(\theta))\mathbf{g}_1 + (1/3)f_1(\theta)\ \mathbf{g}_2$
$(\cos\theta)\vert {}^1/_2\ \pm{}^1/_2\rangle \mp (\sin\theta)\vert {}^3/_2\ \pm{}^1/_2\rangle$	$-D(\lambda + 2{}^1/_2 \tan\theta)$	$(1 + (1/3)f_1(\theta))\mathbf{A}_1$	$-(1/3)f_1(\theta)\ \mathbf{A}_2$	$(1 + (1/3)f_1(\theta))\mathbf{g}_1 - (1/3)f_1(\theta)\ \mathbf{g}_2$

[a] Definition of parameters: $f_1(\theta) = \cos 2\theta - 2(2^{1/2})\sin 2\theta$; $\tan 2\theta = 4(2^{1/2})/(3\lambda - 2)$; $\lambda = J/D$. **A** is the hyperfine coupling tensor; **g** is the **g** tensor; a superscript c denotes the spin-coupled state.

effect of these matrix elements on the **g** and **A** tensors has not been explored except for $S_1 = 1$, $S_2 = {}^1/_2$.[19]

In this paper the cases $S_1 = 1, {}^3/_2, 2, {}^5/_2$ coupled to $S_2 = {}^1/_2$ are considered. The focus is the effect of the coupling of different spin manifolds via the zero-field splitting on the EPR observables, the **g** and **A** tensors. Specific relationships between these tensors in the coupled state and the tensors in the uncoupled states are given. Both tensor quantities turn out to be rather sensitive to the intermanifold coupling. Also presented are the resonance positions (in terms of observed g values) for selected spin states. When the intermanifold matrix elements are sizable, the observed g values along the major axes do not correspond to the principal components of the molecular **g** tensor so that care must be taken when interpreting EPR spectra, particularly the spectra of randomly oriented samples.

It should be noted that strictly speaking **g** and **A** are matrix quantities, not tensor quantities.[20] However, in this work axial symmetry is assumed in all cases so that the matrices do transform as tensors so that the common usage of referring to **g** and **A** as tensors will be retained.

Results

The spin Hamiltonian used to describe the pair of coupled spins includes exchange and zero-field-splitting terms.

$$H = H_{\text{ex}} + H_{\text{zfs}}$$

The exchange Hamiltonian is assumed to contain only the isotropic Heisenberg term while the zero-field splitting is assumed to have axial symmetry

$$H_{\text{ex}} = JS_1 \cdot S_2$$

$$H_{\text{zfs}} = D^S[S_z{}^2 - (1/3)S(S + 1)]$$

where J is the exchange constant and D^S is the zero-field-splitting constant for spin manifold S. The assumption of axial symmetry implies that all tensor quantities are collinear. In this work, $S_2 = {}^1/_2$ in all cases so that the entire zero-field splitting arises only from S_1. In the general experimental situation the symmetry may be lower than axial, but analytical expressions cannot be obtained for the rhombic case. Nonetheless, the results presented here are still useful because they could be used as the starting point in a perturbation calculation to account for a nonaxial case. The exchange Hamiltonian couples the individual spins to give spin states of $S = S_1 + S_2, S_1 + S_2 - 1, ..., |S_1 - S_2|$ with $J < 0$ being ferromagnetic and $J > 0$ being antiferromagnetic. The total spin states $|S\ M_s\rangle$ form the basis set for the total Hamiltonian and can be found from the uncoupled single spin states as

$$|S\ M_s\rangle = \sum_{m_{s_1}} |m_{s_1} m_{s_2}\rangle\langle S_1 S_2 m_{s_1} m_{s_2}|SM_s\rangle$$

where $|m_{s_1} m_{s_2}\rangle = |S_1 m_{s_1} S_2 m_{s_2}|$ is the determinant of the single spin states and $\langle S_1 S_2 m_{s_1} m_{s_2}|SM_s\rangle$ is the Clebsch-Gordon coefficient. This basis set is diagonal in H_{ex} but H_{zfs} has nonzero elements of the form $\langle S'M_s|H_{\text{zfs}}|SM_s\rangle$. These matrix elements arise from the single-state zero-field splittings and are due to the state mixing caused by the exchange term. If S were a good quantum number these terms would be zero for the coupled Hamiltonian but in this work only M_s is a good quantum number. The total Hamiltonian is then diagonalized to give the final wave functions. In all the cases considered in this paper, the Hamiltonian matrix can be factored into 2×2 blocks and each block is diagonalized as described in the appendix.

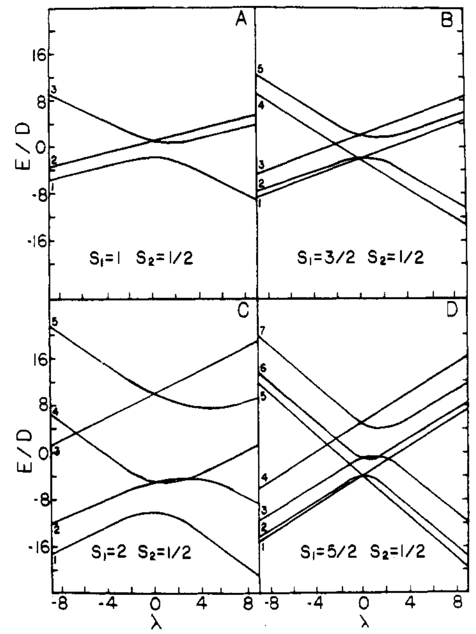

Figure 1. Reduced energies (E/D) plotted as a function of $\lambda = J/D$. The definition of D varies for each spin-coupled system and is given in the text. The primary contributing basis function ($|S\ M_s\rangle$) for each energy level changes for $\lambda < 0$ and $\lambda > 0$. For each system the primary basis function is identified from lowest energy to highest energy. (A) $S_1 = 1$, $S_2 = {}^1/_2$. For $\lambda < 0$: 1, $|{}^3/_2\ \pm{}^1/_2\rangle$; 2, $|{}^3/_2\ \pm{}^3/_2\rangle$; 3, $|{}^1/_2\ \pm{}^1/_2\rangle$. For $\lambda > 0$: 1, $|{}^1/_2\ \pm{}^1/_2\rangle$; 3, $|{}^3/_2\ \pm{}^1/_2\rangle$; 2, $|{}^3/_2\ \pm{}^3/_2\rangle$. (B) $S_1 = {}^3/_2$, $S_2 = {}^1/_2$. For $\lambda < 0$: 1, $|2\ 0\rangle$; 2, $|2\ \pm1\rangle$; 3, $|2\ \pm2\rangle$; 4, $|1\ 0\rangle$; 5, $|1\ \pm1\rangle$. For $\lambda > 0$: 4, $|1\ 0\rangle$; 2, $|1\ \pm1\rangle$; 1, $|2\ 0\rangle$; 5, $|2\ \pm1\rangle$; 3, $|2\ \pm2\rangle$. (C) $S_1 = 2$, $S_2 = {}^1/_2$. For $\lambda < 0$: 1, $|{}^5/_2\ \pm{}^1/_2\rangle$; 2, $|{}^5/_2\ \pm{}^3/_2\rangle$; 3, $|{}^5/_2\ \pm{}^5/_2\rangle$; 4, $|{}^3/_2\ \pm{}^1/_2\rangle$; 5, $|{}^3/_2\ \pm{}^3/_2\rangle$. For $\lambda > 0$: 1, $|{}^3/_2\ \pm{}^1/_2\rangle$; 2, $|{}^3/_2\ \pm{}^3/_2\rangle$; 4, $|{}^5/_2\ \pm{}^1/_2\rangle$; 5, $|{}^5/_2\ \pm{}^3/_2\rangle$; 3, $|{}^5/_2\ \pm{}^5/_2\rangle$. (D) $S_1 = {}^5/_2$, $S_2 = {}^1/_2$. For $\lambda < 0$: 1, $|3\ 0\rangle$; 2, $|3\ \pm1\rangle$; 3, $|3\ \pm2\rangle$; 4, $|3\ \pm\ 3\rangle$; 5, $|2\ 0\rangle$; 6, $|2\ \pm\ 1\rangle$; 7, $|2\ \pm2\rangle$. For $\lambda > 0$: 5, $|2\ 0\rangle$; 2, $|2\ \pm1\rangle$; 3, $|2\ \pm2\rangle$; 1, $|3\ 0\rangle$; 6, $|3\ \pm1\rangle$; 7, $|3\ \pm2\rangle$; 4, $|3\ \pm3\rangle$.

The resultant wave functions are used to relate the observables of the EPR experiment, the **g** and **A** tensors in the coupled system, to their origins from the uncoupled spins. The Hamiltonians in the coupled (H_c') and uncoupled (H_u') representations are

$$H_c' = \beta B \cdot \mathbf{g}^c \cdot S + S \cdot \mathbf{A}_1{}^c \cdot I_1 + S \cdot \mathbf{A}_2{}^c \cdot I_2$$

$$H_u' = \beta B \cdot \mathbf{g}_1 \cdot S_1 + \beta B \cdot \mathbf{g}_2 \cdot S_2 + S_1 \cdot \mathbf{A}_1 \cdot I_1 + S_2 \cdot \mathbf{A}_2 \cdot I_2$$

where β is the Bohr magneton, B is the applied magnetic field, and I is the nuclear spin operator. Application of the Wigner–Eckart theorem to the matrix elements of these Hamiltonians easily allows for the calculation of the relationships between the tensors in the coupled and uncoupled representations.

The $S_1 = 1$, $S_2 = {}^1/_2$ spin system gives rise to two states, $S = {}^3/_2$ and $S = {}^1/_2$. Zero-field splitting occurs only in the $S = {}^3/_2$ manifold so a single parameter, $D = D^{3/2}$, describes the system. The Wigner–Eckart theorem gives the relationship between the total zero-field splitting, D, and the single-spin zero-field splitting, D_1, as

$$D = (1/3)D_1$$

The results for the energies of the various states and the rela-

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Table II. Results for $S_1 = {}^3/_2$, $S_2 = {}^1/_2$[a]

state	energy	$\mathbf{A}_1{}^c$	$\mathbf{A}_2{}^c$	$\mathbf{g}^c$
$\lvert 2\ \pm 2\rangle$	$(1/4)D(3\lambda + 8)$	$(3/4)\mathbf{A}_1$	$(1/4)\mathbf{A}_2$	$(3/4)\mathbf{g}_1 + (1/4)\mathbf{g}_2$
$(\cos\theta)\lvert 2\ \pm 1\rangle \pm (\sin\theta)\lvert 1\ \pm 1\rangle$	$(1/4)D(3\lambda - 4 + 4(3^{1/2})\tan\theta)$	$(1 - (1/4)f_{3/2}(\theta))\mathbf{A}_1$	$(1/4)f_{3/2}(\theta)\ \mathbf{A}_2$	$(1 - (1/4)f_{3/2}(\theta))\mathbf{g}_1 + (1/4)f_{3/2}(\theta)\ \mathbf{g}_2$
$\lvert 2\ 0\rangle$	$(1/4)D(3\lambda - 8)$			
$(\cos\theta)\lvert 1\ \pm 1\rangle \mp (\sin\theta)\lvert 2\ \pm 1\rangle$	$-(1/4)D(5\lambda - 4 + 4(3^{1/2})\tan\theta)$	$(1 + (1/4)f_{3/2}(\theta))\mathbf{A}_1$	$-(1/4)f_{3/2}(\theta)\ \mathbf{A}_2$	$(1 + (1/4)f_{3/2}(\theta))\mathbf{g}_1 - (1/4)f_{3/2}(\theta)\ \mathbf{g}_2$
$\lvert 1\ 0\rangle$	$-(1/4)D(5\lambda + 8)$			

[a] Definition of parameters: $f_{3/2}(\theta) = \cos 2\theta - 3^{1/2}\sin 2\theta$; $\tan 2\theta = (3^{1/2})/(\lambda - 1)$; $\lambda = J/D$. **A** is the hyperfine coupling tensor; **g** is the **g** tensor; a superscript c denotes the spin-coupled state.

Table III. Results for $S_1 = 2$, $S_2 = {}^1/_2$[a]

state	energy	$\mathbf{A}_1{}^c$	$\mathbf{A}_2{}^c$	$\mathbf{g}^c$
$\lvert {}^5/_2\ \pm{}^5/_2\rangle$	$D(\lambda + 10)$	$(4/5)\mathbf{A}_1$	$(1/5)\mathbf{A}_2$	$(4/5)\mathbf{g}_1 + (1/5)\mathbf{g}_2$
$(\cos\theta_2)\lvert {}^5/_2\ \pm{}^3/_2\rangle \pm (\sin\theta_2)\lvert {}^3/_2\ \pm{}^3/_2\rangle$	$D(\lambda - 2 + 6\tan\theta_2)$	$(1 - (1/15)f_2(\theta_2))\mathbf{A}_1$	$(1/15)f_2(\theta_2)\ \mathbf{A}_2$	$(1 - (1/15)f_2(\theta_2))\mathbf{g}_1 + (1/15)f_2(\theta_2)\ \mathbf{g}_2$
$(\cos\theta_1)\lvert {}^5/_2\ \pm{}^1/_2\rangle \pm (\sin\theta_1)\lvert {}^3/_2\ \pm{}^1/_2\rangle$	$D(\lambda - 8 + 6^{1/2}\tan\theta_1)$	$(1 - (1/5)f_2(\theta_1))\mathbf{A}_1$	$(1/5)f_2(\theta_1)\ \mathbf{A}_2$	$(1 - (1/5)f_2(\theta_1))\mathbf{g}_1 + (1/5)f_2(\theta_1)\ \mathbf{g}_2$
$(\cos\theta_2)\lvert {}^3/_2\ \pm{}^3/_2\rangle \mp (\sin\theta_2)\lvert {}^5/_2\ \pm{}^3/_2\rangle$	$-(1/2)D(3\lambda - 14 + 12\tan\theta_2)$	$(1 + (1/15)f_2(\theta_2))\mathbf{A}_1$	$-(1/15)f_2(\theta_2)\ \mathbf{A}_2$	$(1 + (1/15)f_2(\theta_2))\mathbf{g}_1 - (1/15)f_2(\theta_2)\ \mathbf{g}_2$
$(\cos\theta_1)\lvert {}^3/_2\ \pm{}^1/_2\rangle \mp (\sin\theta_1)\lvert {}^5/_2\ \pm{}^1/_2\rangle$	$-(1/2)D(3\lambda + 14 + 2(6^{1/2})\tan\theta_1)$	$(1 + (1/5)f_2(\theta_1))\mathbf{A}_1$	$-(1/5)f_2(\theta_1)\ \mathbf{A}_2$	$(1 + (1/5)f_2(\theta_1))\mathbf{g}_1 - (1/5)f_2(\theta_1)\ \mathbf{g}_2$

[a] Definition of parameters: $f_2(\theta_1) = \cos 2\theta_1 - 2(6^{1/2})\sin 2\theta_1$; $f_2(\theta_2) = 3\cos 2\theta_2 - 4\sin 2\theta_2$; $\tan 2\theta_1 = 4(6^{1/2})/(5\lambda - 2)$; $\tan 2\theta_2 = 24/(5\lambda - 18)$; $\lambda = J/D$. **A** is the hyperfine coupling tensor; **g** is the **g** tensor; a superscript c denotes the spin-coupled state.

tionships between the **g** tensor and the hyperfine tensors in the coupled and uncoupled regimes are given in Table I. The wave functions in this system only depend on the ratio $\lambda = J/D$ while the energies can be found in terms of λ and D. A plot of the reduced energies (E/D) as a function of λ are given in Figure 1A.

Two of the states here are $M_s = {}^1/_2$ Kramers doublets and should be EPR active if occupied. The resonance positions in each of these doublets treated as pseudo spin ${}^1/_2$ along the major axes can be easily found and are given in terms of observed g values ($g^{\mathrm{obsd}} = \hbar\omega/\beta B_{\mathrm{obsd}}$)

$$g_z^{\mathrm{obsd}} = (1/3)g_{1z}(3 \mp f_1(\theta)) \pm (1/3)g_{2z}f_1(\theta)$$

$$g_x^{\mathrm{obsd}} = (1/6)g_{1x}(9\cos 2\theta - f_1(\theta)) \pm (1/6)g_{2x}(3 \pm f_1(\theta))$$

where the upper sign is for the (primarily) $\lvert {}^3/_2 \pm {}^1/_2\rangle$ doublet and the lower sign is for the (primarily) $\lvert {}^1/_2 \pm {}^1/_2\rangle$ doublet. The expression for g_y^{obsd} can be found by substituting y for x in the g_x^{obsd} equations. The angle θ is found from

$$\tan 2\theta = \frac{4(2^{1/2})}{3\lambda - 2}$$

and the function $f_1(\theta)$ is

$$f_1(\theta) = \cos 2\theta - 2(2^{1/2})\sin 2\theta$$

Interdoublet transitions are also possible if $|J|$ and $|D|$ are small enough, but these g values have not been calculated. It should be noted that the observed g values (such as found in the spectrum of a randomly oriented sample) do not correspond to the molecular tensor values for a given spin state except in the limit of very large $|\lambda|$. However, the molecular **g** tensor can readily be found if g_1, g_2, and $f_1(\theta)$ can be estimated. A plot of $f_1(\theta)$ as a function of λ is given in Figure 2A. Notice that $f_1(\theta)$ changes rather slowly with λ and does not reach asymptotic values until $|\lambda| >> 0$ (not shown in the figure).

If the $\lvert {}^3/_2 \pm {}^3/_2\rangle$ state is the ground state ($\lambda > 0$, $D < 0$) and is isolated from the other states with respect to the magnetic resonance experiment ($\hbar\omega > |D(2^{1/2}\tan\theta - 2)|$), then this state can also be treated as a pseudo spin ${}^1/_2$ Kramers doublet. This gives observed g values of

$$g_z^{\mathrm{obsd}} = 2g_{1z} + g_{2z} \qquad g_x^{\mathrm{obsd}} = g_y^{\mathrm{obsd}} = 0$$

Coupling spins $S_1 = {}^3/_2$ and $S_2 = {}^1/_2$ gives spin states $S = 2$ and $S = 1$, both of which may have zero-field splitting. The zero-field splitting constants, D^S, are found in terms of the single-spin zero-field splitting, D_1, as

$$D^2 = (1/2)D_1 \qquad D^1 = (3/2)D_1$$

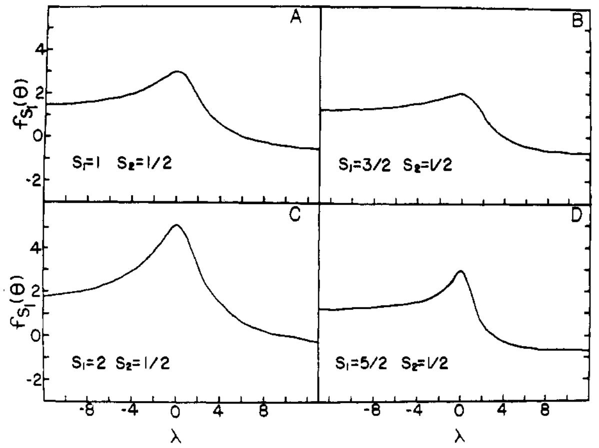

Figure 2. Plots of $f_{s_1}(\theta)$ vs. $\lambda = J/D$. The definitions for $f_{s_1}(\theta)$, θ, and D vary for each spin-coupled system and are given in the text.

For convenience, all terms are defined in terms of the single parameter $D = D^2 = (1/3)D^1$. The results for this coupled spin system are given in Table II. The reduced energies (E/D) are plotted as a function of $\lambda = J/D$ in Figure 1B.

No $M_s = {}^1/_2$ doublets exist for the $S_1 = {}^3/_2$, $S_2 = {}^1/_2$ coupled system. The EPR transitions most likely to be observed (assuming $|D|$ is small enough) are $\lvert S\ 0\rangle$ to (primarily) $\lvert S\ \pm 1\rangle$. The resonance positions along the z axis are easy to find, but along x or y all $\lvert S\ M_s\rangle$ states are coupled and analytical formulas have not been found. The z axis resonance for $\lvert 2\ 0\rangle \leftrightarrow \lvert 2\ \pm 1\rangle$ is

$$g_z^{\mathrm{obsd}} = D'(1 + 3^{1/2}\tan\theta) + (1/4)g_{1z}(4 - f_{3/2}(\theta)) + (1/4)g_{2z}f_{3/2}(\theta)$$

while for $\lvert 1\ 0\rangle \leftrightarrow \lvert 1\ \pm 1\rangle$ it is

$$g_z^{\mathrm{obsd}} = D'(3 - 3^{1/2}\tan\theta) + (1/4)g_{1z}(4 + f_{3/2}(\theta)) - (1/4)g_{2z}f_{3/2}(\theta)$$

where $D' = D/\beta B_{\mathrm{obsd}}$. The rotation angle θ is defined by

$$\tan 2\theta = \frac{3^{1/2}}{\lambda - 1}$$

while

$$f_{3/2}(\theta) = \cos 2\theta - 3^{1/2}\sin 2\theta$$

The function $f_{3/2}(\theta)$ is quite sensitive to λ and is plotted in Figure 2B.

Table IV. Results for $S_1 = {}^5/_2$, $S_2 = {}^1/_2$[a]

state	energy	$\mathbf{A}_1^{\mathrm{c}}$	$\mathbf{A}_2^{\mathrm{c}}$	$\mathbf{g}^{\mathrm{c}}$
$\vert 3\ \pm 3\rangle$	$(5/4)D(\lambda + 4)$	$(5/6)\mathbf{A}_1$	$(1/6)\mathbf{A}_2$	$(5/6)\mathbf{g}_1 + (1/6)\mathbf{g}_2$
$(\cos\theta_1)\vert 3\ \pm 2\rangle \pm (\sin\theta_1)\vert 2\ \pm 2\rangle$	$(1/4)D(5\lambda + 4(5^{1/2})\tan\theta_1)$	$(1 - (1/12)f_{5/2}(\theta_1))\mathbf{A}_1$	$(1/12)f_{5/2}(\theta_1)\ \mathbf{A}_2$	$(1 - (1/12)f_{5/2}(\theta_1))\mathbf{g}_1 + (1/12)f_{5/2}(\theta_1)\ \mathbf{g}_2$
$(\cos\theta_2)\vert 3\ \pm 1\rangle \pm (\sin\theta_2)\vert 2\ \pm 1\rangle$	$(1/4)D(5\lambda - 12 + 4(2^{1/2})\tan\theta_2)$	$(1 - (1/6)f_{5/2}(\theta_2))\mathbf{A}_1$	$(1/6)f_{5/2}(\theta_2)\ \mathbf{A}_2$	$(1 - (1/6)f_{5/2}(\theta_2))\mathbf{g}_1 + (1/6)f_{5/2}(\theta_2)\ \mathbf{g}_2$
$\vert 3\ 0\rangle$	$(1/4)D(5\lambda - 16)$			
$(\cos\theta_1)\vert 2\ \pm 2\rangle \mp (\sin\theta_1)\vert 3\ \pm 2\rangle$	$-(1/4)D(7\lambda - 16 + 4(5^{1/2})\tan\theta_1)$	$(1 + (1/12)f_{5/2}(\theta_1))\mathbf{A}_1$	$-(1/12)f_{5/2}(\theta_1)\ \mathbf{A}_2$	$(1 + (1/12)f_{5/2}(\theta_1))\mathbf{g}_1 - (1/12)f_{5/2}(\theta_1)\ \mathbf{g}_2$
$(\cos\theta_2)\vert 2\ \pm 1\rangle \mp (\sin\theta_2)\vert 3\ \pm 1\rangle$	$-(1/4)D(7\lambda + 8 + 4(2^{1/2})\tan\theta_2)$	$(1 + (1/6)f_{5/2}(\theta_2))\mathbf{A}_1$	$-(1/6)f_{5/2}(\theta_2)\ \mathbf{A}_2$	$(1 + (1/6)f_{5/2}(\theta_2))\mathbf{g}_1 - (1/6)f_{5/2}(\theta_2)\ \mathbf{g}_2$
$\vert 2\ 0\rangle$	$-(1/4)D(7\lambda + 16)$			

[a] Definition of parameters: $f_{5/2}(\theta_1) = 2\cos 2\theta_1 - 5^{1/2}\sin 2\theta_1$; $f_{5/2}(\theta_2) = \cos 2\theta_2 - 2(2^{1/2})\sin 2\theta_2$; $\tan 2\theta_1 = 2(5^{1/2})/(3\lambda - 4)$; $\tan 2\theta_2 = 2(2^{1/2})/(3\lambda - 1)$; $\lambda = J/D$. **A** is the hyperfine coupling tensor; **g** is the **g** tensor; a superscript c denotes the spin-coupled state.

Each doublet state could be treated as an isolated, pseudo spin ${}^1/_2$ state. However, since M_s is integral in each case and thus likely to give short relaxation times, these resonances are not likely to be observed so the calculation of the observed g values has not been done.

The $S_1 = 2$, $S_2 = {}^1/_2$ coupled spin system gives rise to total spins $S = {}^5/_2$ and $S = {}^3/_2$, both of which may zero-field split. In terms of the single-spin zero-field splitting, D_1, the parameters $D^{5/2}$ and $D^{3/2}$ are found to be

$$D^{5/2} = (3/5)D_1 \qquad D^{3/2} = (7/5)D_1$$

Here the single parameter $D = (1/5)D_1 = (1/3)D^{5/2} = (1/7)D^{3/2}$ is used to characterize the zero-field splitting of the coupled spin system. The results are summarized in Table III. The reduced energies are plotted as a function of $\lambda = J/D$ in Figure 1C.

Both the "S" $= {}^5/_2$ and "S" $= {}^3/_2$ manifolds have $M_s = \pm{}^1/_2$ doublets that, if occupied, should be EPR active. The observed intradoublet g values along the major axes are given by

$$g_z^{\text{obsd}} = (1/5)g_{1z}(5 \mp f_2(\theta_1)) \pm (1/5)g_{2z}f_2(\theta_1)$$

$$g_x^{\text{obsd}} = (1/10)g_{1x}(25\cos 2\theta_1 - f_2(\theta_1)) \pm (1/10)g_{2x}(5 \pm f_2(\theta_1))$$

where the upper sign is for the (primarily) $|{}^5/_2\ \pm{}^1/_2\rangle$ doublet and the lower sign is for the (primarily) $|{}^3/_2\ \pm{}^1/_2\rangle$ doublet. The expression for g_y^{obsd} can be found by substituting y for x in the g_x^{obsd} equations. The angle θ_1 is found from

$$\tan 2\theta_1 = \frac{4(6^{1/2})}{5\lambda - 2}$$

and the function $f_2(\theta_1)$ is

$$f_2(\theta_1) = \cos 2\theta_1 - 2(6^{1/2})\sin 2\theta_1$$

This function is plotted vs. λ in Figure 2C.

The $M_s = \pm{}^5/_2$ and $M_s = \pm{}^3/_2$ doublets can also be treated as pseudo spin ${}^1/_2$ Kramers doublets. If the resonance for each doublet is assumed to be isolated, then the observed g values for $M_s = \pm{}^5/_2$ are

$$g_z^{\text{obsd}} = 4g_{1z} + g_{2z}$$

$$g_x^{\text{obsd}} = g_y^{\text{obsd}} = 0$$

and for $M_s = \pm{}^3/_2$ are

$$g_z^{\text{obsd}} = (1/5)g_{1z}(15 \mp f_2(\theta_2)) \pm (1/5)g_{2z}f_2(\theta_2)$$

$$g_x^{\text{obsd}} = g_y^{\text{obsd}} = 0$$

where the upper sign is for $S = {}^5/_2$ ($\lambda << 0$) and the lower sign is for $S = {}^3/_2$ ($\lambda << 0$). The characteristic function $f_2(\theta_2)$ is given by

$$f_2(\theta_2) = 3\cos 2\theta_2 - 4\sin 2\theta_2$$

and the angle θ_2 is found from

$$\tan 2\theta_2 = \frac{24}{5\lambda - 18}$$

The final system to be considered is $S_1 = {}^5/_2$ and $S_2 = {}^1/_2$. These spins couple to give states $S = 3$ and $S = 2$, each of which is subject to zero-field splitting. In terms of the single-spin zero-field splitting, D^3 and D^2 are

$$D^3 = (2/3)D_1 \qquad D^2 = (4/3)D_1$$

The single parameter used to describe the zero-field splitting here is $D = D^3 = (1/2)D^2$. The results for this system are given in Table IV. The reduced energies (E/D) are plotted as a function of λ in Figure 1D.

The important EPR transitions for this system are likely to occur from $M_s = 0$ to $M_s = \pm 1$. Only the resonance positions along the z axis can easily be found and are given by

$$g_z^{\text{obsd}} = D'(1 + 2^{1/2}\tan\theta_2) + (1/6)g_{1z}(6 - f_{5/2}(\theta_2)) + (1/6)g_{2z}f_{5/2}(\theta_2)$$

for "S" = 3 and by

$$g_z^{\text{obsd}} = D'(2 - 2^{1/2}\tan\theta_2) + (1/6)g_{1z}(6 + f_{5/2}(\theta_2)) - (1/6)g_{2z}f_{5/2}(\theta_2)$$

for "S" = 2 and again $D' = D/\beta B_{\text{obsd}}$. The off-diagonal coupling gives θ_2 from

$$\tan 2\theta_2 = \frac{2(2^{1/2})}{3\lambda - 1}$$

and

$$f_{5/2}(\theta_2) = \cos 2\theta_2 - 2(2^{1/2})\sin 2\theta_2$$

This function is plotted against λ in Figure 2D.

Here again, each doublet state has integral M_s so that observed g values have not been calculated within the context of an isolated pseudo spin ${}^1/_2$.

Discussion

The results presented here give analytical formulas for EPR parameters in spin-coupled systems including the interaction between different spin manifolds. This latter effect is usually ignored with the justification that the exchange energy is much larger than the zero-field splitting energy. This assumption is usually not warranted since even for the cases of $|J| >> |D|$ the various $f(\theta)$ values deviate significantly from the $D = 0$ values. This means that observable perturbations in the **g** and **A** tensors should be detectable.

An example using these results is in order. Buluggiu[3] has reported detailed EPR data on the nickel(II)-doped aquodichloro(pyridine *N*-oxide)copper(II) dimeric complex. This complex has pairs of $S = {}^1/_2$ Cu^{2+} ions antiferromagnetically coupled so that at low temperatures only the $S = 0$ state is occupied. This allows for the observation of the resonance of the Ni^{2+}–Cu^{2+} pairs, an example of an $S_1 = 1$, $S_2 = {}^1/_2$ coupled spin system. Buluggiu[3] reports molecular **g** and **A** tensor data for both the (primarily) $|{}^1/_2\ \pm{}^1/_2\rangle$ and the (primarily) $|{}^3/_2\ \pm{}^1/_2\rangle$ manifolds: for "S" = ${}^1/_2$ (the ground state), $g_x^{\mathrm{c}} = 2.639$, $g_y^{\mathrm{c}} = 2.452$, $g_z^{\mathrm{c}} = 2.127$,

$A_z^c(\mathrm{Cu}^{2+}) = 40 \times 10^{-4}$ cm^{-1}; for "S" = $^3/_2$, $g_x^c = 2.345$, g_y^c = 2.307, $g_z^c = 2.205$, $A_z^c(\mathrm{Cu}^{2+}) = 44 \times 10^{-4}$ cm^{-1}. Kokoszka et al.[18] report the **g** and **A** tensor parameters for this complex doped with diamagnetic Zn^{2+}. This gives the EPR parameters for the isolated Cu^{+2} in the same environment as in the coupled system: $g_{2x} = 2.056$, $g_{2y} = 2.083$, $g_{2z} = 2.306$, and $A_{2z} = 139 \times 10^{-4}$ cm^{-1}. This allows for the calculation of the $\mathbf{g}_1$ tensor and the J/D ratio. Inspection of Table I shows that the average of $\mathbf{g}$("S" = $^3/_2$, M_s = $\pm^1/_2$) and $\mathbf{g}$("S" = $^1/_2$, M_s = $\pm^1/_2$) gives $\mathbf{g}_1$ (this is truly independent of the size of λ). The data result in $g_{1x} = 2.492$, g_{1y} = 2.379, and $g_{1z} = 2.166$. Further, since the sign of the hyperfine coupling constant cannot be determined from the EPR spectrum, A_2^c("S" = $^3/_2$, $M_s = \pm^1/_2$) = A_2^c("S" = $^1/_2$, $M_s = \pm^1/_2$), which, within experimental error, is as observed. From the values for $\mathbf{g}_1$, $\mathbf{g}_2$, $\mathbf{g}^c$, A_{2z}, and A_{2z}^c, five independent measures of the quantity $f_1(\theta)$ are found. The average of these five values is $f_1(\theta) = 0.88$. This gives $\lambda = +45$ or $\lambda = +3.2$. The correct choice for λ cannot be ascertained from this data, but J and D must have the same sign. The ground state is (primarily) $|^1/_2\ \pm^1/_2\rangle$, implying $J >$ 0, so that $D > 0$ is also true. The important conclusion is that even when $|\lambda|$ is quite large (in this case it is possible that $J = 45D$) the EPR data is sensitive enough to observe the perturbations caused by the intermanifold coupling.

This example illustrates the need to consider coupling between spin manifolds when the EPR of spin-coupled systems is interpreted. Buluggiu[3] attributed the small deviation between the observed $\mathbf{A}_2^c$ and the predicted $\mathbf{A}_2^c$ to supertransferred spin density between the nickel and copper ions; the calculations presented here show that the interaction between spin manifolds does equally well in accounting for $\mathbf{A}_2^c$. In addition, the **g** tensor values are also consistently predicted. The sensitivity of the g values to the off-diagonal interaction is large: in the example presented here, if $\lambda = +45$, the ground state would be primarily $|^1/_2\ \pm^1/_2\rangle$ with only 2% admixture of $|^3/_2\ \pm^1/_2\rangle$, yet a significant and easily observable effect on the **g** tensor is noted. In general, unless $|J|$ $> 50|D|$, perturbations in the **g** tensor due to the coupling of spin manifolds will be observed.

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Appendix

Consider the system with basis set $|1\rangle$ and $|2\rangle$. The matrix elements of the Hamiltonian H are

$$\langle 1|H|1\rangle = H_{11}$$

$$\langle 2|H|2\rangle = H_{22}$$

$$\langle 1|H|2\rangle = \langle 2|H|1\rangle = V$$

This system diagonalizes to give energies

$$E_\mathrm{a} = H_{11} + V \tan\theta$$

$$E_\mathrm{b} = H_{22} - V \tan\theta$$

with wave functions

$$|a\rangle = (\cos\theta)|1\rangle + (\sin\theta)|2\rangle$$

$$|b\rangle = -(\sin\theta)|1\rangle + (\cos\theta)|2\rangle$$

where the rotation angle θ is defined by

$$\tan 2\theta = \frac{2V}{H_{11} - H_{22}}$$

Some useful relationships are

$$E_\mathrm{a} - E_\mathrm{b} = \frac{2V}{\sin 2\theta}$$

$$\cos 2\theta = (H_{11} - H_{22})[(H_{11} - H_{22})^2 + 4V^2]^{-1/2}$$

$$\sin 2\theta = 2V[(H_{11} - H_{22})^2 + 4V^2]^{-1/2}$$

$$\cos\theta = \pm[(1/2)[H_{11} - H_{22}][(H_{11} - H_{22})^2 + 4V^2]^{-1/2} + 1/2]^{1/2}$$

$$\sin\theta = \pm[(1/2)[H_{22} - H_{11}][(H_{11} - H_{22})^2 + 4V^2]^{-1/2} + 1/2]^{1/2}$$

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Electronic Ground States and Spectra of Square-Planar Nickel(II) Complexes with Aromatic Dithiocarboxylato Ligands

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The electronic structure and related properties of five nickel(II) complexes of chelating aromatic dithiocarboxylato ligands have been investigated by means of EHMO–SCCC calculations. Overlap populations, two-center energy terms, and computed atomic charges were found to provide adequate information on the mechanism of the π-back-bonding effect. The role of sulfur 3d AO's was revealed to be unimportant in determining the bonding mode. The trimeric nature of the complexes in the solid state in a "skewed-sandwich" form and their ability to form adducts with Lewis bases as well as their sulfur addition reactions affording perthio complexes by chelate ring expansion are explained in view of the energies and characters of the frontier MO's. Correlation of the electronic spectral data with calculated electronic transitions facilitated the characterization of all the observed bands for the square-planar $\mathrm{NiS_4}$ chromophores. The Δ_1 values related to ligand field strength were calculated from the energies of the ligand field states, taking into account configuration interaction with reasonable values for the interelectronic repulsion parameters. These values were found to be in excellent agreement with the positions of the 1,1-dithio ligands in the spectrochemical series.

Introduction

The electronic structure of square-planar complexes of Ni(II) with sulfur-containing conjugated ligands has attracted considerable interest.[1-6] Particular emphasis has been placed upon the interpretation of the observed electronic properties of these compounds with respect to their highly delocalized covalent bonding. Simple molecular orbital methods of the extended-Hückel[7-10] LCAO–MO–SCF type[11] as well as more sophisticated molecular calculations of the INDO–SCF–CI[12] and ab initio type[13] have

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