the alkyl substituent effect (relative to X = H) on the acidity of either HA or of BH^+, the ρ_α values are negative for neutral acids but positive for BH^+ acids.[2,7]

Unconjugated heteroatom or unsaturated carbon atom substituents give rise to substituent field/inductive effects (*F*).[7b] The *F* effects can be removed through the use of the dual parameter relationship: $-\delta\Delta G° = c + \sigma_\alpha\rho_\alpha + \sigma_F\rho_F$, where ρ_α and ρ_F are the corresponding reaction constants. Values of the required σ_F parameters have been independently evaluated under conditions appropriate to the gas phase.[4b,5d,12] The use of this equation is shown for two typical gas-phase acidity series in Figure 1 (open circle points). The applicability and precision of fit of σ_α values for heteroatom and unsaturated carbon substituents are illustrated for these by the linear relationships which result from plotting $-\delta\Delta G°_g - \sigma_F\rho_F$ vs. corresponding σ_α values.[15,16]

The ρ_F and ρ_α values given in Figure 1 show the expected trends resulting from increased distances of separation. In full papers the widespread utility of this approach will be reported.

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(12) Values of σ_F used are zero for all alkyl substituents and for others: C_6H_5, 0.10; CH_3OCH_2, 0.12; HCF_2, 0.34; CF_3, 0.44; CN, 0.60, $Si(CH_3)_3$, -0.02; $H_2C{=}CH$, 0.06; $HC{\equiv}C$, 0.23; CCl_3, 0.44; $N(CH_3)_2$, 0.10. Values of σ_α for CH_3OCH_2, HCF_2, c-C_6H_{11}, and 1-adamantyl have been estimated.

(13) The result shown in Figure 1 that $1.00 \neq \rho_\alpha(XCH_2SH_2^+)/\rho_\alpha(XCH_2SH) = 1.6$ does not support the previous attempt[14] to evaluate *P* and *F* effects of alkyl substituents.

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(15) Deviations of the open circle points from the regression lines, of course, include errors in the $\sigma_F\rho_F$ as well as $\sigma_\alpha\rho_\alpha$ relationships.

(16) Values of $-\Delta G°_g$ for HA acidities which are not given in ref 3, 4, or 18 have been obtained as described in ref 4b.

(17) Values of $-\delta\Delta G°_g$ for BH^+ acidity not previously reported have been obtained by using the methods described in the following references: (a) Wolf, J. F.; Staley, R. G.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417. (b) Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *Ibid.* **1978**, *100*, 240. (c) Bromilow, J.; Abboud, J. L. M.; Lebrilla, C. B.; Taft, R. W.; Scorrano, G.; Lucchini, V. *Ibid.* **1981**, *103*, 5448.

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Creutz–Taube Ion: A Model for the EPR *g* Tensor Which Includes the Bridging Ligand

Jaeju Ko, Li-Tai Zhang, and Mary Jo Ondrechen*

Department of Chemistry, Northeastern University
Boston, Massachusetts 02115

Received October 7, 1985

The Creutz–Taube ion, a pyrazine-bridged mixed-valence dimer of ruthenium, $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$, has been the center of controversy for the last 17 years.[1-9] One important piece of its puzzle which must be accounted for is the observed anisotropy of the EPR g tensor.[1-8] Here we report the first model to predict successfully the components of the *g* tensor which also includes essential features of the pyrazine bridging ligand.

We adopt a three-site, purely electronic model Hamiltonian given by

$$\hat{H}_{\text{eff}} = \hat{H}_{\text{cov}} + \sum_k (\hat{H}_{\text{tet}}{}^k + \hat{H}_\rho{}^k + \hat{H}_{\text{SO}}{}^k) \quad (1)$$

$$\hat{H}_{\text{cov}} = \sum_\mu \alpha|\pi^{*\mu}\rangle\langle\pi^{*\mu}| + \sum_k\sum_\mu J\{|xz_k{}^\mu\rangle\langle\pi^{*\mu}| + |\pi^{*\mu}\rangle\langle xz_k{}^\mu|\} \quad (2)$$

$$\hat{H}_{\text{tet}}{}^k = (D/3)(\hat{L}_z{}^2 - {}^1\!/_3 L(L+1))_k \quad (3)$$

$$\hat{H}_\rho{}^k = (E/12)(\hat{L}_+{}^2 + \hat{L}_-{}^2)_k \quad (4)$$

$$\hat{H}_{\text{SO}}{}^k = \xi(\hat{L}_z\hat{S}_z + {}^1\!/_2\hat{L}_+\hat{S}_- + {}^1\!/_2\hat{L}_-\hat{S}_+)_k \quad (5)$$

where $\hat{H}_{\text{cov}}$ contains the strong coupling between one π^* state on the bridging ligand and the $4d_{xz}$ orbitals on the two Ru ions. *J* is the coupling constant for this interaction and α is the energy gap between the parent π^* state and the parent $4d_{xz}$ orbitals. μ is the spin index (+ or −) and *k* (=L or R) labels the left and right Ru ion orbitals. *D* is the tetragonal splitting, *E* the rhombic splitting, and ξ the spin-orbit coupling.[10]

Spin-orbit coupling on the bridge is neglected and the π^* state is assumed to be orthogonal to all of the Ru 4d orbitals. $\hat{H}_{\text{cov}}$ is taken to be of the one-electron type, and only $|xz_L\rangle$ and $|xz_R\rangle$ are assumed to be coupled via the bridging ligand.

Of the five Hamiltonian parameters α, *J*, *D*, *E*, and ξ, we calculate four of these—α, *J*, *D*, and *E*—from a first-principles MO calculation by the HFS–DVM method.[11] The values for the parameters correspond to a delocalized (D_{2h}) ground state.[9] Since this is a spin-polarized calculation, different values for the parameters are obtained for spin up ↑ and spin down ↓ electrons. Each parameter was obtained by averaging the values found for L↑, L↓, R↑, and R↓ Ru electrons in the converged ground state. The results are given in the last column of Table I. The nonrelativistic HFS–DVM does not give the spin-orbit coupling ξ. This we take as our one fit parameter.

The MO calculations[11,12] have shown that the basis orbitals $|xz_L\rangle$, $|\pi^*\rangle$, and $|xz_R\rangle$ form linear combinations resembling the bonding, nonbonding, and antibonding MO's of the Hückel allyl radical, and we label them $|B\rangle$, $|N\rangle$, and $|A\rangle$. In the mixed-valence species, the $|N\rangle$ state is half-occupied. We diagonalize eq 2 and write expressions for the three energy gaps ($E_A - E_N$), ($E_N - E_B$), and ($E_A - E_B$) in terms of the two parameters α and *J*. Using the numerical values for these energy gaps obtained from the converged ground state in our MO calculation, we solve for α and *J* with two of them and the third provides a check.

From standard methods,[10] we obtain the components of the *g* tensor as matrix elements of the ground-state Kramers doublet states. Values for the spin-orbit coupling in the range ξ = 600–750 cm^{-1} give qualitatively reasonable *g* values. Our best fit was obtained for ξ = 690 cm^{-1}. Table I compares the experimental *g* values with those obtained from the present and previous models.

We caution that our tetragonal splitting, albeit reasonable, should not be taken too seriously. It is of the order of the error in the HFS–DVM procedure. We have tried a series of values for the tetragonal splitting in the range $|D|$ = 0–800 cm^{-1}. For D = −800 cm^{-1}, the corresponding g values are qualitatively reasonable (g_x and g_y change by 10–15%, while g_z stays the same).

The best fit value for the spin-orbit coupling, 690 cm^{-1}, is smaller than that calculated earlier for the Ru^{3+} ion (1200 cm^{-1})[13] and somewhat smaller than the value of 1000 cm^{-1} used in previous models of this type. In part, this can be accounted for by the

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Table I. Parameters and g Values for the Present and Previous Models[a]

ref	6	5	4	7,1[c]	7,1[d]	8	present work
tetragonal splitting	−945	$D + E =$	−843.8	−2317	+600	−800	$D = -330$
rhombic splitting		+2400	+109.2	−745	−2690	+1600	$E = -2000$
spin–orbit coupling	−1050	+1050	+1000	−1000	−1000	+1000	$\xi = +690$
$\hat{H}_{el}$[e]			$\epsilon_1 = 0.0$			$\epsilon_1 = 2870$	$\alpha = 10000$
			$\epsilon_2 = 2900$			$\epsilon_2 = 3250$	$J = -6400$
			$\epsilon_3 = 0.0$			$\epsilon_3 = 2120$	
g_x		1.334[b]	[f]	1.346[b]		1.36	1.36
g_y		2.779[b]		2.799[b]		2.81	2.85
g_z		2.489[b]		2.487[b]		2.50	2.45
coord system	single ion	symmetry-adapted single ion	dimer	symmetry-adapted single ion	dimer[d]	dimer	dimer

[a] All energies in cm^{-1}. [b] Experimental g values. [c] Original numbers used symmetry-adapted single-ion coordinates. [d] Translated into dimer coordinates to facilitate comparison with other treatments. Tetragonal and rhombic splittings muxt be in the same coordinate system for meaningful comparison. [e] ϵ_1, ϵ_2, and ϵ_3 are defined in ref 8 in terms of their symmetries; they are given approximately by $\epsilon_1 \simeq \langle x^2 - y^2{}_L|\hat{H}_{el}|x^2 - y^2{}_R\rangle$, $\epsilon_2 \simeq \langle xz_L|\hat{H}_{el}|xz_R\rangle$, and $\epsilon_3 \simeq \langle yz_L|\hat{H}_{el}|yz_R\rangle$. Note that previous treatments postulate direct coupling between metal d orbitals on the left- and right-hand ions; the bridge is not explicitly included. [f] Fitted g values not reported.

Table II. Optical Absorption (OA) and MCD Transitions[a]

predicted			observed[16,2a,17]		
energy, cm^{-1}	polarization	assignment	energy, cm^{-1}	polarization	assignment
5 700	z	bonding → nonbonding or "IT"	6 500, m	z	IT, OA
15 000	z	nonbonding → antibonding	18 200, m		$t_{2g} \rightarrow \pi^*$, OA
16 000, w	z	$4d_{x^2-y^2}$ → antibonding, s			
17 000, w	z	$4d_{yz}$ → antibonding, s			
16 000	x	$4d_{x^2-y^2}$ → antibonding, l	17 400		MCD
17 000	x	$4d_{yz}$ → antibonding, l	20 400		MCD
1 500	$x + y$	$4d_{x^2-y^2}$ → nonbonding	~2 000, br		MCD
2 300	$x + y$	$4d_{yz}$ → nonbonding	~4 000, br		MCD
[b]			12 800		MCD, OA, w

[a] w = weak; s = a minor component; l = a major component; m = frequency maximum; br = broad. [b] Not predicted by our model. Might be attributed to doublet → quartet transition.[2a]

effects of delocalization. Delocalization of electron density onto ligands reduces the effective spin–orbit coupling by 20–30% for the 3d subshell.[14]

Of course there are approximations and sources of error in this calculation. Probably the most significant of these are the neglect of spin–spin exchange and the neglect of e$^-$–e$^-$ repulsion. The parameters obtained from the HFS–DVM calculation probably carry at least 10% error and nearly ±100% for the tetragonal splitting.

Even with these approximations, this model makes some very important points. We have shown how to incorporate essential features of the bridging ligand into the g-tensor problem. Although we have only one fit parameter, we have successfully calculated three components of the g tensor.

Our model may be used to predict energies of optical transitions, but with the parameters used here these predictions are only approximate. The EPR g tensor is a property of the electronic ground state. Because of electronic relaxation effects, the electronic parameters (α, J, D, and E) for the ground and for each excited state are different. We have used ground-state parameters here and this introduces errors into the transition energies calculated from differences between eigenvalues. These predicted transitions are given in Table II. We can indeed account for the observed optical absorption (OA) and MCD features,[16,2a,17] although our transition energies are too low by 15–20% (and only qualitative at very low energies).[18]

Because the strong through-bridge coupling causes the $|B\rangle$ state to be shifted far (in energy) from the pure Ru 4d orbitals, the IT transition ($|B\rangle \rightarrow |N\rangle$) is not broadened by spin–orbit and low-site-symmetry effects. These effects lead to extra transitions, but not near the IT band.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank the Arthur D. Little Foundation for an Arthur D. Little Fellowship awarded to Jaeju Ko. We are grateful to Professor P. N. Schatz for a copy of ref 8 prior to its publication.

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(18) More accurate transition energies have been obtained from transition operator calculations.[11]

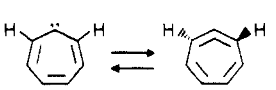
Triplet Ground-State Cycloheptatrienylidene

Robert J. McMahon[†] and Orville L. Chapman*

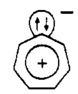
Department of Chemistry and Biochemistry
University of California—Los Angeles
Los Angeles, California 90024

Received June 24, 1985

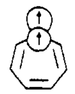
The role of cycloheptatrienylidene (**1**) in the arylcarbene rearrangements remains unclear.[1] Early trapping studies suggested equilibration of **1** and **2**, although this is now in question.[2]



1 2



1a



1b

[†] National Science Foundation Graduate Fellow (1980–1983). IBM Corporation Graduate Fellow (1983–1984). UCLA Distinguished Scholar (1984–1985).

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