

Communications

Electronic Excitation MO Assignment of $\text{Rh}_2(\text{O}_2\text{CR})_4(\text{L}_{\text{ax}})_2$ Using MCD Experiment and Theory

Sir:

The electric-dipole allowed absorption band that occurs in $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds¹⁻⁴ at 550–600 nm ($17\text{--}18 \times 10^3 \text{ cm}^{-1}$, $\epsilon_{\text{max}} \approx 240 \text{ M}^{-1} \text{ L}^{-1}$) with x,y polarization, has been assigned (by different workers) in two ways, viz., $\pi^*(\text{Rh}_2) \rightarrow \sigma^*(\text{Rh}_2)^{1,2}$ and $\pi^*(\text{Rh}_2) \rightarrow \sigma^*(\text{Rh-O})^3$ (Figure 1). For $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{OH}_2)_2$ (complex **1**· $2\text{H}_2\text{O}$), this band (hereafter called band A) was first assigned by Dubicki and Martin (DM)⁵ to $\pi^*(\text{Rh}_2) \rightarrow \sigma^*(\text{Rh}_2)$, or $5e_g \rightarrow 4a_{2u}$, on the basis of its x,y linear polarization, temperature independence of its intensity, and the relatively high sensitivity of this absorption band energy to axial ligand variation. Norman and Kolari (NK)² then reported SCF-X α -SW ground-state MO calculations for $\text{Rh}_2(\text{O}_2\text{CH})_4(\text{OH}_2)_2$ that could be used to better understand the spectrum of **1**· $2\text{H}_2\text{O}$; i.e., they provided for consideration several MOs near the HOMO and LUMO. Next, Martin et al. (MWRFF)¹ published further evidence supporting the previously proposed DM assignment ($^1\text{A}_1 \rightarrow ^1\text{E}$) by showing that the x,y -static electric dipole and MO nature predicted theoretically² for band A were consistent with the results obtained from their single-crystal polarized absorption spectroscopy study. In addition, MWRFF¹ also observed a 297-cm⁻¹ vibronic progression on band A ($\approx 552 \text{ nm}$) of **1**· $2\text{H}_2\text{O}$. This progression was attributed to $\nu(\text{Rh}_2)$ of their $^1\text{E}(e_g^2 a_{2u}^1)$ electronic excited state, since 320 cm⁻¹⁶ was earlier believed to be $\nu(\text{Rh}_2)$ of the ground state for **1**· $2\text{H}_2\text{O}$. The direction of this 23-cm⁻¹ shift is consistent with the assigning of band A to $\pi^*(\sim\text{Rh}_2) \rightarrow \sigma^*(\sim\text{Rh}_2)$ or $5e_g \rightarrow 4a_{2u}$ (D_{4h}). Shortly thereafter Norman et al. (NRC)⁷ also published excited-state SCF-X α -SW computational results corresponding to the MWRFF excited ^1E assignment of configuration $e_g^2 a_{2u}^1$ for band A. The degeneracy of this excited state and the similar experimental and calculated state energy differences were supportive of the MWRFF assignment for A. Subsequently, the polarized crystal spectra of **1**· $2\text{H}_2\text{O}$ were remeasured and extended by Miskowski et al. (MSSSG),³ since it was felt that (a) a 320-cm⁻¹ vibration of the ground state was too high for $\nu(\text{Rh}_2)$ but about right for the symmetric Rh-O(carboxylato) stretching mode, and that (b) for a $\pi^*(\sim\text{Rh}_2) \rightarrow \sigma^*(\sim\text{Rh}_2)$ type assignment (MWRFF¹ and NK, NRC^{2,6}) to be correct for the $18.1 \times 10^3 \text{ cm}^{-1}$ (552 nm) band A, the 23-cm⁻¹ difference between

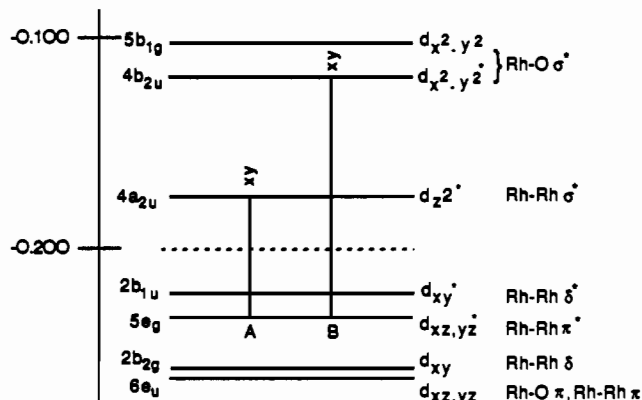


Figure 1. Partial MO diagram for $\text{Rh}_2(\text{O}_2\text{CH})_4(\text{OH}_2)_2$ in hartrees (1 hartree = 27.21 eV), with A and B being the assignments of MWRFF¹-NK² and MSSSG,³ respectively. The present MCD results directly confirm assignment A.

$\nu(\text{Rh}_2)$ values for the ground state and this excited state is too small. In this same study the resonance-enhanced Raman solution spectrum of complex $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCCH}_3)_2$ was also reported. For a band at ca. 345 cm⁻¹, the measured polarization ($\rho = 0.12$) was closer to that of $\nu(\text{Rh-O})$ ($a_{1g}, \rho_{x,y} = 0.125$) than to the computed ρ of $\nu(\text{Rh}_2)$ ($a_{1g}, \rho_z = 0.333$),⁸ and they assigned $\nu(\text{Rh}_2)$ to the only other low-energy band observed (170 cm⁻¹). On this basis together with points a and b above, as well as the computational results of NK,² MSSSG³ reassigned band A to $\pi^*(\sim\text{Rh}_2) \rightarrow \sigma^*(\sim\text{Rh-O})$, or $5e_g \rightarrow 4b_{2u}$ (D_{4h}). Next there appeared a new electronic ground state vibrational study of complex $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ by Flint et al. (FHC).⁹ Their Raman, resonance Raman (RR), and Raman polarizations of isotopically (¹⁶O, ¹⁸O, CH₃, CD₃) substituted solids were all consistent with assigning bands at 289 and 338 cm⁻¹ to, respectively, $\nu(\text{Rh}_2)$ and $\nu(\text{Rh-O})$ for their complex, $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$, but no bands were found in the 150–170-cm⁻¹ region where the $\nu(\text{Rh}_2)$ band was previously suggested to be.³ Most recently Miskowski et al. (MDCMSW)¹⁰ chose various $\text{Rh}_2(\text{carboxylato})_4(\text{L}_{\text{ax}})_2$ complexes that they take to have accessible $\sigma(\sim\text{Rh-L}) \rightarrow \sigma^*(\sim\text{Rh}_2)$ electronic transitions (to nondegenerate excited states) in order to measure RR band depolarization ratios. MDCMSW concluded, as did CHF⁹ and MWRFF,¹ that $\nu(\text{Rh}_2)$ was in the 300-cm⁻¹ region.

With a view to providing some new and, we hoped, decisive experiment to distinguish between the two possible assignments, each having strong merit, of band A, we undertook the study of it by MCD experiment and theory and report the results now.

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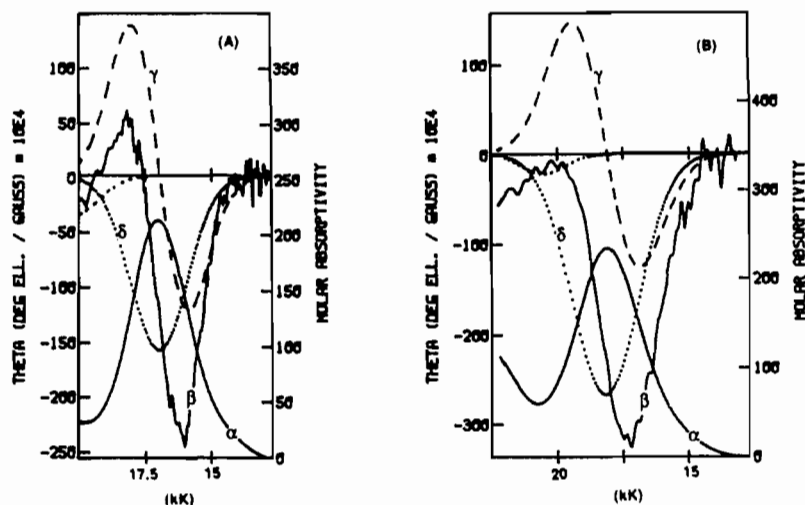


Figure 2. EAS (α) and MCD (β) spectra and corresponding deconvoluted A (γ) and B terms (δ) for (A) $\text{Rh}_2(\text{D-mandelato})_4(\text{EtOH})_2$ and (B) $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2$.

MCD spectra were recorded and calibrated by using the monochromator of a JASCO ORD/CD instrument and digital CD electronics¹¹ of our design. The light beam was collimated, plane polarized, and alternately left and right circularly polarized by a Photoelastic Modulator (PEM) at 50294 Hz. The resulting beam passed through a cuvette containing the sample solution subjected to a longitudinal magnetic field and was detected by using a Hamamatsu R-376 PMT (-20°C). The output signal of the PMT was phase detected and amplified by a lock-in amplifier, the signal then being collected and stored with a micro-computer. In addition to collecting the spectral data the micro-computer also controlled the monochromator, PEM amplitude, and PMT high-voltage power supply in a feedback loop. The electronic absorption spectra were obtained with a Varian 2300 spectrophotometer. By calibration the two wavelength axes were matched throughout.

Electronic absorption spectra (EAS) and MCD spectra for the compound $\text{Rh}_2(\text{D-mandelato})_4(\text{EtOH})_2$ (complex **2-2EtOH**) in ethanol and $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{NCCH}_3)_2$ (compound **1-2NCMe**) in acetonitrile were obtained at room temperature. (Isomer D is also *R*, *l*, or +.) These and deconvoluted MCD A and B terms for the compounds **2-2EtOH** and **2-2NCMe** are shown in Figure 2. The dipole strength, \bar{D}_0 (0.104 and 0.126 D^2 for **2-2EtOH** and **1-2NCMe**), for band A and the corresponding solution MCD \bar{A}_1 and \bar{B}_0 parameters (in the order **2-2EtOH** then **1-2NCMe**, $\bar{A}_1 = 0.073$ and 0.100 D^2 and $\bar{B}_0 = -5.0 \times 10^{-5}$ and $-9.3 \times 10^{-5} \text{ D}^2 \text{ cm}$) were obtained by careful deconvolution with Gaussian bands to obtain A , B , and D parameters of earlier definition.¹² These parameters¹² were converted to \bar{A}_1 , \bar{B}_0 , and \bar{D}_0 .¹³ The same EAS and MCD band centers, $\epsilon^{\text{EAS}} = \epsilon^{\text{MCD}}$, and bandwidth parameters, $\text{FWHM}_{\text{EAS}} = 2(\ln 2)^{1/2} \Delta_{\text{MCD}}$, were used.¹³

Optical band A maximizes at 16.9×10^3 and $18.0 \times 10^3 \text{ cm}^{-1}$, respectively, for compounds **2-2EtOH** and **1-2NCMe**. This band shift ($\sim 17\text{--}18 \times 10^3 \text{ cm}^{-1}$) is attributed to axial ligand substitution of O-coordinated EtOH for N-coordinated NCCH₃. The sensitivity of band A is not the result of variation of the bridging carboxyl groups but is due to L_{ax} substitution, since very similar shifts are observed for the EtOH and NCCH₃ adducts when the D-mandelato bridge¹¹ is replaced by the acetato bridge.⁴ The molar absorptivity corresponding to band A for compound **2-2EtOH** and **1-2NCMe** are 212 and 225 $\text{M}^{-1} \text{ L}^{-1}$, respectively.

Corresponding to band A in the EAS is a net negative band in the MCD spectra of both compounds **2-2EtOH** and **1-2NCMe**, but the minima are at significantly lower energies than EAS maxima (Figure 1). Deconvolution of the MCD spectra requires a positive A term (and $\bar{A}_1 = +$) and a negative B term (and \bar{B}_0

$= -$). \bar{A}_1/\bar{D}_0 ratios for compounds **2-2EtOH** and **1-2NCMe** are 0.70 and 0.80, respectively.

The presence of the A term for band A is consistent with a ${}^1A_1 \rightarrow {}^1E$ assignment of, for our molecules, any transition type $e_{g(u)} \rightarrow \gamma_{u(g)}$ or $\gamma_{u(g)} \rightarrow e_{g(u)}$, where γ can be $a_1, a_2, b_1,$ or b_2 . Such transitions would have x,y polarization, and this is, indeed, the dominant polarization found for band A from single-crystal spectroscopy of the similar complex **1-2H₂O**.¹³ Knowing the 1E excited state symmetry, or 1E_u in D_{4h} , and the experimentally determined sign and magnitude of \bar{A}_1/\bar{D}_0 , one now must decide between the assignments of MWRF,¹ $5e_g \rightarrow 4a_{2u}$, and MSSSG,³ $5e_g \rightarrow 4b_{2u}$. For these ${}^1A_{1g} \rightarrow {}^1E_u$ transitions, use of the most recent formalism¹³ yields in reduced matrix element form our MCD parameter

$$\bar{A}_1 = \left(\sum_{ijk=-1}^1 (\epsilon_{ijk})(\text{MCD}_{ijk} \text{ factor}) \frac{\{A\}}{3\mu_B|A|} \|\mu^{f'}\| \begin{Bmatrix} f'_i & f_j & f_k \\ A^* & J^* & J^* \end{Bmatrix} \times \right. \\ \left. \|\mu^{f'}\| \|\mu^{f''}\| \right) \text{D}^2 \quad (1)$$

where $\|\mu^{f'}\| = \langle {}^1E || \mu^{f'} || {}^1E \rangle$, $\|\mu^{f''}\| = \langle {}^1A || \mu^{f''} || {}^1E \rangle$, $\|\mu^{f'''}\| = \langle {}^1E || \mu^{f'''} || {}^1A \rangle$, and $\mu_z = -\mu_B L_z$ and $\{ \}$ is a $6j$ symbol. Expanding the above summation, followed by explicit irreducible representation substitution (ground state, excited state and operators), evaluating the resulting $6j$ coefficients, and evaluating the MCD factors in complex basis yield

$$\bar{A}_1 = \frac{1}{3(\sqrt{2}\mu_B)} \|\mu^{f'}\| \|\mu^{f''}\| \|\mu^{f'''}\| \text{D}^2 \quad (2)$$

Our EAS electric dipole strength in this formalism is

$$\bar{D}_0 = \frac{\{A\}}{3|A|} \sum_{i=-1}^1 \left(\frac{1}{|f_j|} \delta(A^* f_j J) \{A^* f_j J\} \|\mu^{f'}\| \|\mu^{f''}\| \right) \text{D}^2 \quad (3)$$

After the summation was expanded, followed by explicit substitution of appropriate irreducible representations and evaluation of the $2j$ and $3j$ phases, \bar{D}_0 becomes $1/3 \|\mu^{f'}\| \|\mu^{f''}\|$, so that the final ratio is

$$\frac{\bar{A}_1}{\bar{D}_0} = \frac{1}{\sqrt{2}} \langle {}^1E || L^{A_{2u}} || {}^1E \rangle \quad (4)$$

which is to be compared to $[\bar{A}_1(\text{exp})/\bar{D}_0(\text{exp})]$. With further evaluation of the reduced matrix element, substituting the appropriate MO types proposed, we obtain

$$\frac{\bar{A}_1}{\bar{D}_0} = + \frac{1}{\sqrt{2}} \langle e_g, \pi^*(\sim \text{Rh}_2) || L^{A_{2u}} || e_g, \pi^*(\sim \text{Rh}_2) \rangle \quad (5)$$

for MWRF,¹ and for MSSSG³ the sign of (5) is negative. Un-

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reducing the matrix elements yields, for MWRF

$$\frac{\bar{A}_1}{\bar{D}_0} = -\langle e_g(y), \pi^*(\sim Rh_2) | \hat{A}_{2g} | e_g(x), \pi^*(\sim Rh_2) \rangle \quad (6)$$

and for MSSSG the opposite sign.

It is noteworthy that for both the MWRF and MSSSG assignments, evaluation of \bar{A}_1/\bar{D}_0 involves computing identical multicenter integrals, but the signs of \bar{A}_1/\bar{D}_0 ratios are opposite. MO phases were carefully matched with all other computational features. $\langle \ell_z \rangle$ was evaluated in the all-center operator AO matrix mode^{11,14} for $Rh_2(O_2CH)_4$. Bond distances and angles,¹⁵ AO single- ζ 2s and 2p functions for C and O,¹⁶ and $\zeta = 1.2$ for 1s H¹⁷ were from the literature. Rh 5p (double- ζ) and 5s (triple- ζ) functions are our renormalized outermost terms of more complex functions,¹⁸ and the 4d (triple- ζ) function is from the literature.¹⁸ Basis orbital energies from the literature were used (2s, 2p C, O from ref 19; 1s H is -13.6 eV; for Rh 4d, 5s, 5p the VOIPS of Co 3d, 4s, 4p^{19,20} were used with 10 000 cm^{-1} subtracted from each.²¹ The 100 functions were used to compute the 70×70 S and L_z matrices,^{14,22} and subsequently the MO C matrix,²⁰ all on an IBM 3081 (Triangle University Computing Center). We obtain $\bar{A}_1/\bar{D}_0 = +0.985$ for the MWRF assignment, $5e_g \rightarrow 4a_{2u}$, which matches the experimental \bar{A}_1/\bar{D}_0 sign and is in good agreement with the experimental magnitudes for 1-2NCMe and 2-2EtOH and consistent with the $\pi^*(\sim Rh_2) \rightarrow \sigma^*(\sim Rh_2)$ excitation.

The circular dichroism spectra of two $Rh_2(O_2CR)_4L_2$ compounds ($RCO_2 = L$ -mandelate and $L = EtOH$; $RCO_2 = D$ -methoxyphenylacetate and $L = THF$) have been reported and shown to be consistent with the MSSSG assignment,²³ which was at that time generally accepted. However, these data are also consistent with the MWRF assignment.²⁴ The all-center operator matrix treatment of the CD vicinal effect of $Rh_2(D$ -mandelato)₄ will be published elsewhere.¹¹

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Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27695

Jack W. Trexler, Jr.
Anton F. Schreiner*

Department of Chemistry and Laboratory
for Molecular Structure and Bonding
Texas A&M University
College Station, Texas 77843

F. Albert Cotton

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An Organometallic Route to Micron-Sized Whiskers of Zinc Sulfide

Sir:

A number of technologies require the development of high-performance optical materials that also meet stringent specifications of optical transparency and thermal, chemical, and mechanical properties.^{1,2} For example, an infrared-transmitting



Figure 1. Transmission electron micrograph of the solid product formed upon reacting $[EtZn(SBu^1)]_2$ with H_2S at a flow rate of 5 cm^3/min in CH_2Cl_2 solution at 22 $^{\circ}C$.

window material should have low thermal expansion, high melting and decomposition temperatures, chemical inertness to hydrolysis and oxidation, and high fracture toughness. One of the most attractive materials for many IR optical applications is ZnS,³ but this material, as presently fabricated, does not possess the required mechanical properties.

One approach to improving the mechanical properties of a material is to form a self-similar composite,⁴⁻⁶ in this case, ZnS whiskers in a polycrystalline ZnS matrix. To fabricate IR-transmitting ZnS/ZnS composites, it would be necessary to use micron-sized whiskers of ZnS that have length to width ratios (aspect ratios) greater than 10. No present methodology exists for the convenient, large-scale preparation of such whiskers, although larger single crystals and whiskers of ZnS have been made by a variety of high-temperature (>900 $^{\circ}C$), generally vapor-phase, routes.⁷⁻¹⁶ We have sought alternative methods for producing ZnS whiskers that would give greater control over the product morphology. Low-temperature organometallic routes are attractive for this purpose, and we report herein a novel route to

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