Strength and Trans Influence of the Rh-Rh Bond in Rhodium(II) Carboxylate Dimers

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Abstract: SCF-Xα-SW calculations of $Rh_2(O_2CH)_4(H_2O)_2$ and $Rh_2(O_2CH)_4$ are used to discuss the electronic structures of rhodium(II) carboxylates, $Rh_2(CO_3)_4^{4-}$, $Rh_2(SO_4)_4^{4-}$, and Rh_2^{4+}(aq). The Rh-Rh bonds in these compounds are predicted to be single, not triple; the basic orbital configuration is $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$. Reasons for the short Rh-Rh distance of 2.39 Å in $Rh_2(O_2CCH_3)_4(H_2O)_2$ are discussed in this context. Both a detailed description and a simple orbital picture of how the Rh-Rh bond so dramatically weakens the trans Rh-OH_2 bonds are given; the key is the Rh-OH_2 antibonding character of Rh-Rh σ and σ^* orbitals. The converse effect of axial ligands on the Rh-Rh bond is also discussed. Comparisons are made with previous calculations on quadruply bonded complexes, particularly $Mo_2(O_2CH)_4$. The peaks at 17.1, 22.7, 40 sh, and 45.9 $\times$ 10^{-3} cm^{-1} in the electronic spectrum of $Rh_2(O_2CCH_3)_4(H_2O)_2$ are assigned to $\pi^* \rightarrow \sigma^*$, $\pi^* \rightarrow$ Rh-O σ^*, $\sigma \rightarrow \sigma^*$, and L$\sigma \rightarrow \sigma^*$ transitions, respectively. The recently isolated diatomic Rh_2 is predicted to have an $S = 2$ ground state at Rh-Rh = 2.39 Å, based on a "d^1s^1" configuration; comparisons are made to Mo_2. The ground state of $[Ru_2(O_2CR)_4]^+$ compounds is predicted to be $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$.

We have previously analyzed the quadruple metal-metal bonds[1] in $Mo_2Cl_8^{4-}$ and $Mo_2(O_2CH)_4$, and their interactions with metal-ligand bonds, using SCF-Xα-SW calculations.[2,3] Others have reported similar calculations on $Re_2Cl_8^{2-}$ [4] and $Cr_2(O_2CH)_4$;[5] SCF-HF-LCAO treatments of d^4-d^4 dimers are also beginning to appear.[6,7] The combination of the Xα-SW calculations and careful experimental investigations of electronic,[4,8-12] photoelectron,[6,13,14] resonance Raman,[11,15] and EPR[16] spectra have greatly increased understanding of the electronic structures of these important compounds.

The dinuclear M_2L_8 structure of D_{4h} symmetry common to nearly all the d^4-d^4 dimers is also known for a smaller number of compounds where the metals have other d^n configurations.[1] Prominent among these are the carboxylates $M_2(O_2CR)_4L_2$ (L = axial ligand), which have been structurally characterized not only for Cr(II), Mo(II), and Re(III), but also for Ru(2.5),[17] Co(II),[18] Rh(II),[19] and Cu(II).[20] Just as considerable controversy has surrounded the assignment of electronic spectra for the d^4-d^4 dimers, so there has been much discussion of what the metal-metal bond orders are in these latter compounds containing $d^{5.5}$, d^7, and d^9 metals. Indeed the question is the same in both cases: what is the nature and ordering of the orbitals having higher energy than the metal-metal σ, π, and δ *bonding* levels (which are just filled in the d^4-d^4 systems)? The calculations and experiments mentioned above were largely stimulated by, and have essentially settled, this question for the quadruply bonded molecules. We are presently carrying out Xα-SW calculations on Ru(2.5), Rh(II), and Cu(II) carboxylate dimers in hopes of achieving a similar resolution for these systems.

The background of opposing views about the Rh(II) case is as follows. The initial report of the crystal structure of $Rh_2(O_2CCH_3)_4(H_2O)_2$ contained the proposal that a Rh-Rh single bond was present.[21] A later extended-Hückel calculation supported this view, giving the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$, and allowing a consistent interpretation of observed variations in the electronic spectrum upon changing the axial ligands from H_2O to stronger donors.[22] In the meantime, however, Cotton had pointed out that the short Rh-Rh distance, now accurately known as 2.386 (1) Å,[19] was more consistent with a multiple interaction.[19,23] Rh-Rh bonds which are unambiguously single usually have lengths of 2.7-2.8 Å;[1,24] estimates in this range are also obtained using Rh covalent radii derived from metal-ligand distances.[19,25] In particular, he suggested a triple bond, based on the electronic configuration $\sigma^2\pi^4\delta^2\sigma_n^2\sigma_n'^2\delta^{*2}$. The σ_n and σ_n' orbitals are essentially nonbonding $d_{z^2}p_z$ hybrids directed outward from the ends of the metal-metal axis. Although the recent theoretical and experimental work on the d^4-d^4 systems shows these orbitals to be nonexistent in the appropriate energy range, it is not clear whether the same orbital diagram would apply to a d^7-d^7 case.[26]

In this paper we offer conclusions, based on an SCF-Xα-SW treatment of $Rh_2(O_2CH)_4(H_2O)_2$, which we believe go far toward settling this longstanding controversy. Our results should also apply to the complexes $Rh_2(CO_3)_4^{4-}$, $Rh_2(SO_4)_4^{4-}$, and $Rh_2(H_2O)_{10}^{4+}$, whose spectra indicate entirely analogous electronic structures to the carboxylates.[27] We also consider the general phenomenon of the metal-metal trans influence[28] by comparing calculations on $Rh_2(O_2CH)_4(H_2O)_2$ and $Rh_2(O_2CH)_4$. A large number of experimental observations have established that certain ligands produce abnormally weak bonds to metals for other ligands bound trans to them.[29-31] The data suggest that the most influential ligands in this respect are those which form strong, covalent σ bonds to the metal.[32] On this basis, one would expect other metals to be among the strongest trans-influencing ligands. The structures of the dinuclear carboxylates, some of which are summarized in Table I, confirm this hypothesis. As the metal-metal bond strengthens, the metal-axial ligand bond weakens, becoming 0.4-0.6 Å longer than normal when the trans metal is quadruply bonded. Our calculations reveal quantitative details of this phenomenon which translate into a simple qualitative understanding. Finally, we discuss in a preliminary manner the electronic structures of the recently isolated diatomic molecule Rh_2[34] and Ru(2.5) carboxylate dimers.

Computational Section

Atomic coordinates for the calculations of $Rh_2(O_2CH)_4(H_2O)_2$, $Rh_2(O_2CH)_4$, and Rh_2 were all based on the x-ray structure of $Rh_2(O_2CCH_3)_4(H_2O)_2$.[19] Specifically, the bond parameters used were Rh-Rh = 2.39 Å, Rh-O_2CH = 2.04 Å, Rh-OH_2 = 2.31 Å, C-O = 1.27 Å, C-H = 1.08 Å, O-H = 0.99 Å, angle O-C-O = 125°, and angle H-O-H = 120°. The coordinate systems for $Rh_2(O_2CH)_4$ (D_{4h} symmetry) and $Rh_2(O_2CH)_4(H_2O)_2$ (D_{2h} symmetry) are shown below by a perspective drawing and a z-axis projection, respectively.

Overlapping atomic sphere radii were obtained by our nonempirical procedure[35] and are given in Table II. They represent 91.0, 89.3, and 85.0% of the atomic-number radii for

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Table I. Bond Lengths (Å) in Some $M_2(O_2CR)_4L_2$ Compounds (L = Axial Ligand)

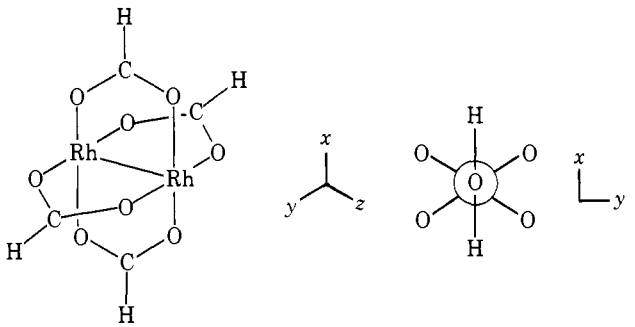
Compd	M-M	M-L	Av M-O(COR)
$Mo_2(O_2CCF_3)_4$[a]	2.090 (4)	2.72 (1)[e]	2.06 (2)
$Mo_2(O_2CCF_3)_4(py)_2$[b]	2.129 (2)	2.548 (8)	2.116 (6)
$Rh_2(O_2CCH_3)_4(H_2O)_2$[c]	2.386 (1)	2.310 (3)	2.039 (3)
$Cu_2(O_2CCH_3)_4(H_2O)_2$[d]	2.615 (1)	2.160 (3)	1.969 (3)

[a] Reference 33. [b] Reference 28. [c] Reference 19. [d] Reference 20. [e] Intermolecular contact to carboxylate oxygen atom.

Table II. Sphere Radii (bohrs)[a] and SCF Charge Distributions (electrons)

	$Rh_2(O_2CH)_4(H_2O)_2$		$Rh_2(O_2CH)_4$		Rh_2	
Region[b]	Radius	Charge	Radius	Charge	Radius	Charge
Rh	2.481	44.26	2.450	44.09	2.503	44.22
O	1.736	7.98	1.703	7.88		
C	1.618	5.23	1.587	5.14		
H	1.316	0.96	1.292	0.93		
O_w	1.774	8.02				
H_w	1.163	0.74				
Intersphere		5.75		6.39		1.15
Extramolecular	8.894	0.18	8.294	0.14	5.064	0.41

[a] 1 bohr = 0.529 177 Å. [b] O and O_w are carboxylate and water oxygen atoms, respectively, and similarly for the hydrogen atoms H and H_w.



$Rh_2(O_2CH)_4(H_2O)_2$, $Rh_2(O_2CH)_4$, and Rh_2, respectively. The percentage for Rh_2 is the same as previously used[36] for Mo_2. We believe that all the radii are within 0.1 bohr of the virial-theorem optimized values, although no effort was made to optimize them fully. The best values for $Rh_2(O_2CH)_4$ would probably be slightly larger than those for $Rh_2(O_2CH)_4(H_2O)_2$, rather than smaller as in the values used. Nothing in our experience suggests that any of the conclusions presented below would be altered by further refinement of the radii.

In other respects the calculations were carried out as previously described[3,36] for $Mo_2(O_2CH)_4$ and Mo_2. Ground-state SCF results were obtained for all three molecules. Since Rh_2 is predicted to be open shell, both spin-restricted and spin-polarized calculations of its lowest energy state were converged. Transition-state calculations were converged in spin-restricted form for the first two ionization energies of $Rh_2(O_2CH)_4(H_2O)_2$, and in spin-polarized form for all the spin- and dipole-allowed spectral transitions of Rh_2.

Results

As for $Mo_2(O_2CH)_4$, the energy-level diagrams for $Rh_2(O_2CH)_4$ and $Rh_2(O_2CH)_4(H_2O)_2$ divide into three basic regions. The 20 essentially unperturbed formate C-H and C-O σ orbitals in the range -1.07 to -0.49 hartree have nearly the same energies in all three molecules. Four water-localized O-H bonding levels also lie in this region for the hydrated complex. In the range -0.43 to -0.21 hartree, $Rh_2(O_2CH)_4$ has 23 oxygen lone pair, C-O π, Rh-O, and Rh-Rh orbitals; two of a_{1g}, and one of a_{2u}, symmetry are found significantly perturbed in the hydrate (where a_{1g} and a_{2u} become a_g and b_{1u}, respectively) by interaction with the axial water molecules. Four additional orbitals appear which correlate with H_2O σ and π lone pairs, the former being strongly mixed with Rh-Rh σ and σ^* functions. Above -0.18 hartree are found five unoccupied levels of Rh-Rh σ^*, Rh-O σ^*, and C-O π^* types, the first being significantly higher in energy in $Rh_2(O_2CH)_4(H_2O)_2$ than in $Rh_2(O_2CH)_4$ due to its simultaneous Rh-OH_2 σ^* character.

Energies and charge distributions for levels in the second and third regions are given in Table III. They are compared with those of free H_2O in Figure 1, with emphasis on levels important for discussion of the strength and trans influence of the Rh-Rh bond. Figure 2 compares the most important metal-metal and metal-water levels of $Rh_2(O_2CH)_4(H_2O)_2$ with their counterparts in $Mo_2(O_2CH)_4$. Wave function contour maps of critical H_2O-Rh-Rh-OH_2 σ and σ^* orbitals appear in Figures 3 and 4. The contours are the same as previously used[2,3] for analogous orbitals in $Mo_2(O_2CH)_4$ and $Mo_2Cl_8^{4-}$. Table IV gives our assignment for the experimentally observed electronic spectrum of rhodium(II) carboxylates.

The SCF-Xα-SW ground state of Rh_2 at Rh-Rh = 2.39 Å was explicitly determined by spin-restricted and spin-polarized calculations of all reasonable configurations. Spin-restricted eigenvalues for the state found to have lowest energy are compared in Figure 5 with those previously calculated[36] for Mo_2 at Mo-Mo = 2.10 Å. Figure 6 depicts the wave function for the interesting $2\sigma_g$ orbital of Rh_2, essentially the 5s bonding combination; the contours are the same as previously used[3] for the analogous orbital in Mo_2. Table V compares the experimentally observed[34] electronic spectrum of Rh_2 with transitions which we calculate in the same energy range at Rh-Rh = 2.39 Å.

The calculated total energies for Rh_2, $Rh_2(O_2CH)_4$, and $Rh_2(O_2CH)_4(H_2O)_2$ are -9371.8434, $-10\,127.0066$, and $-10\,280.9064$ hartrees, respectively. The corresponding virial ratios $-2T/V$ are 1.000 01, 1.000 30, and 1.000 11. Numbers of electrons in the various spatial regions are summarized in Table II.

Discussion

Strength of the Rh-Rh Bond. The calculations predict that the Rh-Rh bond in rhodium(II) carboxylates is single, not

Table III. Upper Valence Energy Levels (hartrees)[a] and Charge Distribution for $Rh_2(O_2CH)_4$ and $Rh_2(O_2CH)_4(H_2O)_2$

$Rh_2(O_2CH)_4$						$Rh_2(O_2CH)_4(H_2O)_2$						
D_{4h} level	Energy[d]	% charge[b] 2Rh	% charge[b] $4O_2CH$	Major Rh basis Fns[c]	Type	D_{2h} level	Energy	% charge[b] 2Rh	% charge[b] $4O_2CH$	% charge[b] $2H_2O$	Major Rh basis Fns[c]	Type
$7e_u$	−0.0075	0	100		C–O π*	$9b_{2u}$	−0.0062	1	97	2		C–O π*
$3b_{2g}$	−0.0105	4	96			$9b_{3u}$	−0.0065	1	97	2		
$5b_{1g}$	−0.1017	57	43	$d_{x^2-y^2}$	Rh–O σ*	$6b_{1g}$	−0.0959	58	42		d_{xy}	Rh–O σ*
$4b_{2u}$	−0.1195	64	36	$d_{x^2-y^2}$*		$5a_u$	−0.1139	66	34		d_{xy}*	
$4a_{2u}$	−0.1756	82	18	d_{z^2}*	Rh–Rh σ*	$8b_{1u}$	−0.1359	78	14	8	d_{z^2}*	Rh–Rh σ*, Rh–OH_2 σ*
$2b_{1u}$[e]	−0.2208	68	32	d_{xy}*	Rh–Rh δ*	$7b_{1u}$[e]	−0.2161	70	30	0	$d_{x^2-y^2}$*	Rh–Rh δ*
$5e_g$	−0.2343	84	16	$d_{xz,yz}$*	Rh–Rh π*	$6b_{3g}$	−0.2218	81	9	10	d_{yz}*	Rh–Rh π*
						$6b_{2g}$	−0.2279	87	13	0	d_{xz}*	
$2b_{2g}$	−0.2581	86	14	d_{xy}	Rh–Rh δ	$9a_g$	−0.2530	87	13	0	$d_{x^2-y^2}$	Rh–Rh δ
$6e_u$	−0.2632	33	67	$d_{xz,yz}$	Rh–O π, Rh–Rh π	$7b_{2u}$	−0.2517	35	33	31	d_{yz}	Rh–O π,Rh–Rh π
						$7b_{3u}$	−0.2614	38	61	0	d_{xz}	
$1a_{1u}$	−0.2803		100		O lone pair	$8a_g$	−0.2680	57	15	28	d_{z^2},s,p_z	Rh–Rh σ,Rh–OH_2 σ*
						$5b_{3g}$	−0.2742	3	27	70		H_2O π lone pair
						$6b_{2u}$	−0.2785	5	42	54		
$4e_g$	−0.2906	11	89		O lone pair	$4a_u$	−0.2811	0	100			O lone pair
$5a_{1g}$	−0.3008	50	50	d_{z^2},s	Rh–O σ, Rh–Rh	$5b_{2g}$	−0.2914	9	91	0		
						$4b_{3g}$	−0.2948	11	77	13		
$3e_g$	−0.3038	11	89		O lone pair	$4b_{2g}$	−0.3055	9	91	0		
						$3b_{3g}$	−0.3061	12	86	2		
$5e_u$	−0.3138	70	30	$d_{xz,yz}$	Rh–Rh π, Rh–Oπ	$6b_{3u}$	−0.3111	65	35	0	d_{xz}	Rh–Rh π,Rh–O π
						$5b_{2u}$	−0.3149	66	27	7	d_{yz}	
$3a_{2u}$	−0.3299	21	79	d_{z^2}*,s*	Rh–O σ,π	$6b_{1u}$	−0.3240	11	77	12	d_{z^2}*,s*	Rh–O σ,π
$3b_{2u}$	−0.3405	26	74	$d_{x^2-y^2}$*		$7a_g$	−0.3355	18	67	15	d,s	
$1b_{1u}$	−0.3533	39	61	d_{xy}*		$3a_u$	−0.3405	24	76		d_{xy}*	
$4a_{1g}$	−0.3561	66	34	d_{z^2}	Rh–Rh σ, Rh–O σ	$5b_{1u}$	−0.3549	37	63	0	$d_{x^2-y^2}$*	
$4b_{1g}$	−0.3589	40	60	$d_{x^2-y^2}$	Rh–O σ	$5b_{1g}$	−0.3577	38	62		d_{xy}	
$1a_{2g}$	−0.3726		100		C–O π	$4b_{1u}$	−0.3712	16	6	78	d_{z^2}*,p_z*	Rh–OH_2 σ,Rh–Rh σ*
						$4b_{1g}$	−0.3738	0	100			C–O π
$4e_u$	−0.3894	1	99			$5b_{3u}$	−0.3917	1	99	0		
						$5b_{2u}$	−0.3917	10199	0			
$1b_{2g}$	−0.4228	17	83	d_{xy}	Rh–OC π	$6a_g$	−0.3932	44	3	53	d_{z^2}	Rh–OH_2 σ,Rh-Rh σ
						$5a_g$	−0.4260	16	84	0	$d_{x^2-y^2}$	Rh–OC π

[a] All levels between −0.497 and −0.005 hartree except for diffuse Rydberg-state orbitals. These occur for $Rh_2(O_2CH)_4(H_2O)_2$ at −0.0602 ($10a_g$), −0.0459 ($8b_{3u}$), −0.0457 ($8b_{2u}$), −0.0432 ($9b_{1u}$), −0.0375 ($11a_g$), −0.0169 ($7b_{2g}$), and −0.0165 ($7b_{3g}$). Only 4–15% of their charge is located within the atomic spheres. A similar pattern is observed for $Rh_2(O_2CH)_4$. [b] *Relative* amounts of charge within the atomic spheres. The only $Rh_2(O_2CH)_4(H_2O)_2$ orbitals with less than 75% of the total charge within the atomic spheres are $9b_{2u}$ and $9b_{3u}$ (37%); the average is 84%. $Rh_2(O_2CH)_4$ is analogous. [c] Spherical harmonic basis functions contributing more than 10% of the Rh charge for important Rh–Rh, Rh–O(COH), and Rh–OH_2 orbitals, listed in order of decreasing importance. All such Rh contributions are more than 73% d except in $7a_g$ and $6b_{1u}$ for $Rh_2(O_2CH)_4(H_2O)_2$, and $5a_{1g}$ for $Rh_2(O_2CH)_4$, where they are ca. 40% s. Note that the difference in coordinate system between the two molecules makes d_{xy} in one analogous to $d_{x^2-y^2}$ *in the other, and vice versa.* d_{xz} means a bonding d_{xz} combination, d_{z^2}* an antibonding d_{z^2} combination, etc. [d] 0.05 hartree has been added to the actual $Rh_2(O_2CH)_4$ eigenvalues. This shift makes the 20 formate-localized orbitals below −0.497 hartree (not tabulated here) essentially coincident with their counterparts in $Rh_2(O_2CH)_4(H_2O)_2$ and $Mo_2(O_2CH)_4$. [e] The highest occupied levels.

multiple. As shown by Figures 1 and 2, only the σ* orbital of the group σ, π, δ, δ*, π*, σ* remains empty. This is the same result one gets by naively adding six electrons to our diagram for $Mo_2(O_2CH)_4$. In moving from Mo to Rh, the M–O σ* and C–O π* orbitals which bracket the Mo–Mo σ* level are destabilized rather than stabilized relative to the metal–metal orbitals (see Figure 1). Moreover, no Rh 5s- or 5p-type orbitals (such as Cotton's σ_n pair) drop into the proper energy range. There is thus nothing to prevent occupation of the δ* and π* orbitals. The labeling of the levels in Figures 1 and 2 as purely "σ", "σ*", etc., is of course an oversimplification; Table III shows their varying amounts of ligand character. Even considering *all* the orbitals of $Rh_2(O_2CH)_4(H_2O)_2$, however, one still finds a net excess of 2.0 Rh–Rh bonding over Rh–Rh antibonding electrons.

Our prediction of a single bond agrees with that made earlier from an extended-Hückel calculation.[22] In some contrast to the extended-Hückel result, our calculated level ordering appears to be completely consistent with the experimental electronic spectrum, as discussed below. We thus feel that we have

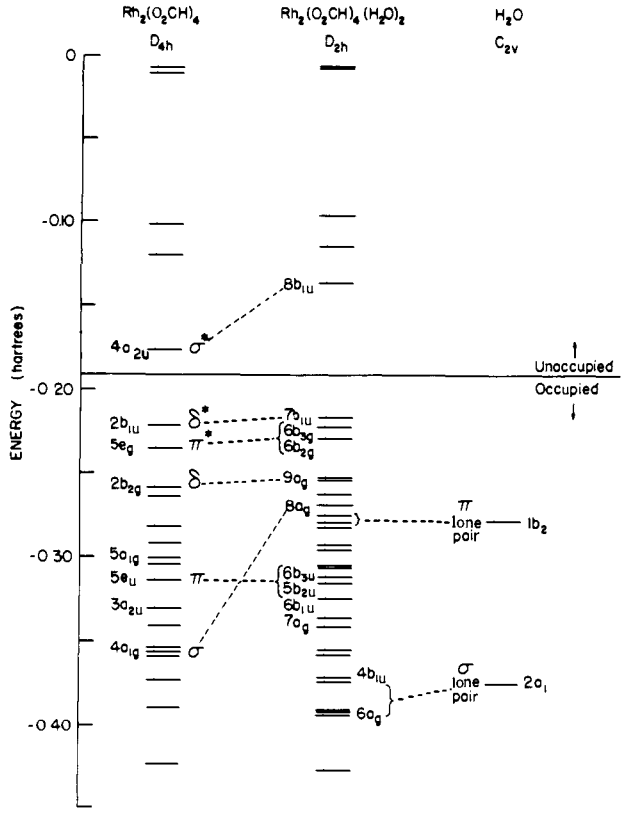


Figure 1. SCF energy levels for $Rh_2(O_2CH)_4$, $Rh_2(O_2CH)_4(H_2O)_2$, and H_2O above −0.49 hartree. The levels which best correlate with the σ, π, δ, δ^*, π^*, and σ^* components of the Rh–Rh bond, and with the in- and out-of-plane water lone pairs, are indicated. Mulliken symbols are given for the Rh–Rh levels, and in addition for all other levels of Rh–Rh and/or Rh–OH_2 σ and σ^* character (a_{1g} and a_{2u} levels for $Rh_2(O_2CH)_4$, a_g and b_{1u} for $Rh_2(O_2CH)_4(H_2O)_2$).

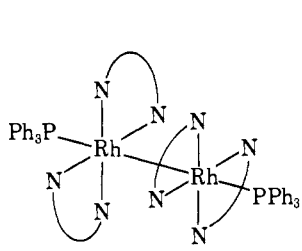
Table IV. Assignment of the Electronic Spectrum of $Rh_2(O_2CCH_3)_4(H_2O)_2$

D_{2h} transition	D_{4h} excited state	Type[a]	Exptl $\tilde{\nu}_{max}$, $cm^{-1} \times 10^{-3}$ [b]
$6b_{3g}, 6b_{2g} \rightarrow 8b_{1u}$	^1E_u	$\pi^* \rightarrow \sigma^*$	17.1 (ϵ 241)
$6b_{3g}, 6b_{2g} \rightarrow 5a_u$	^1E_u	$\pi^* \rightarrow$ Rh–O σ^*	22.7 (ϵ 106)
$8a_g \rightarrow 8b_{1u}$	$^1A_{2u}$	$\sigma \rightarrow \sigma^*$	40 sh (ϵ 4000)
$7a_g \rightarrow 8b_{1u}$	$^1A_{2u}$	$L\sigma \rightarrow \sigma^*$	45.9 (ϵ 17 000)

[a] σ, π, σ^*, and π^* denote the Rh–Rh character of mainly Rh orbitals. Lσ means a mainly formate orbital where the Rh–O(COH) and Rh–Rh interactions are σ. [b] Bond maxima and molar absorptivities in aqueous solution at room temperature, from ref 27.

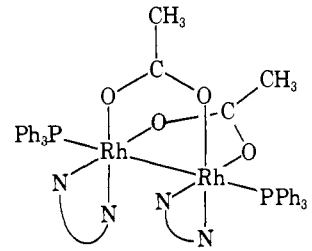
placed the prediction of bond order on a much firmer foundation.

As noted earlier, the observed Rh–Rh distance of 2.39 Å in $Rh_2(O_2CCH_3)_4(H_2O)_2$ seems short for a single bond, by comparison to other known Rh–Rh distances and estimates of covalent radii. One may argue that such covalent radii are well known to be ligand dependent;[37] in particular, most of the known Rh–Rh single bonds occur between metal atoms in lower oxidation states than in the acetate, and thus involve "larger" atoms. However, this effect seems unlikely to account for the entire shortening of the acetate distance from, e.g., that of 2.73 Å in $Rh_4(CO)_{12}$.[38] The natural inference is that the bridging carboxylate ligands constrain the metals to a shorter separation than they would otherwise prefer. The O···O distance in sodium formate is 2.22 Å;[39] this presumably approximates the ideal metal–metal separation from the viewpoint of the formate ligand. Metal–metal distances of 2.09–2.72 Å are known—and can thus be accommodated—within the $M_2(O_2CR)_4$ framework, but this does not prove that these distances would not be different if the C–O distance and/or O–C–O angle were perfectly flexible. The weaker a metal–metal bond, the more likely it is to be affected by ligand preferences.[40]



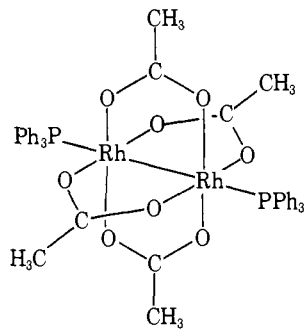
1

$Rh_2(dmg)_4(PPh_3)_2$
Rh–Rh = 2.94 Å[24]



2

$Rh_2(dmg)_2(OAc)_2(PPh_3)_2$
Rh–Rh = 2.62 Å[41]



3

$Rh_2(OAc)_4(PPh_3)_2$
Rh–Rh = 2.45 Å[1]

The three structures below relate to this question. We believe that **1, 2,** and **3** all contain Rh–Rh single bonds. No one has ever asserted otherwise for **1.**[24] Details of the crystal structure strongly support the idea that the ca. 0.2 Å elongation over the usual Rh–Rh distance is due to repulsion between the parallel dimethylglyoximate ligands. To us, this indicates how flexible the Rh–Rh single bond is to such ligand effects. In **2,** we see the dmg–dmg repulsion as approximately balanced by the constraining effect of the bridging acetates, leading to a Rh–Rh distance only a little shorter than normal. The distance in **3** reflects the full constraint of the acetate cage.[42]

Synthesis and structural characterization of Rh_2^{4+} systems with a greater variety of bridging and nonbridging ligands are needed to fully clarify the question of bridge constraint. Our own initial efforts in this direction have not been successful;[43] we hope that the above discussion will stimulate others to work in this area.

Mutual Influence of the Rh–Rh and Rh–OH_2 Bonds. Figure 1 and Table III show that the interaction of H_2O with $Rh_2(O_2CH)_4$ is essentially of σ type. Not only mainly formate levels, but also the π, π^*, δ, and δ^* Rh–Rh orbitals, have nearly identical energies in $Rh_2(O_2CH)_4$ and $Rh_2(O_2CH)_4(H_2O)_2$. The same is true for the water π lone-pair orbitals relative to free water. A contour map of the one Rh–Rh π-type orbital with appreciable H_2O character, $7b_{2u}$, shows that no significant Rh–OH_2 overlap accompanies this mixing. The small amount of H_2O character found in the $6b_{3g}$ (Rh–Rh π^*) orbital, 10%, is quite consistent with results of an EPR study of $Rh_2(O_2CCF_3)_4$–nitroxide adducts.[44]

Table V. Experimental Electronic Spectrum of Rh_2, Compared with Transitions Calculated at Rh–Rh = 2.39 Å

Transition[a]	Calcd energy, $cm^{-1} \times 10^{-3}$	Exptl $\bar{\nu}_{max}$, $cm^{-1} \times 10^{-3}$ [b]
$(2\sigma_g \rightarrow 2\sigma_u)\uparrow$	21.7	
$(1\sigma_g \rightarrow 1\sigma_u)\downarrow$	24.4	
$(1\pi_g \rightarrow 2\sigma_u)\uparrow$	25.2	29.1
$(2\sigma_g \rightarrow 2\pi_u)\uparrow$	25.3	30.8
$(1\pi_g \rightarrow 2\pi_u)\uparrow$	29.8	31.5
$(1\delta_g \rightarrow 2\pi_u)\downarrow$	34.8	32.1
$(1\delta_g \rightarrow 2\pi_u)\uparrow$	39.3	

[a] All spin- and dipole-allowed transitions between 17 and 44 × 10^{-3} cm^{-1}. Vertical arrows indicate whether levels involved are spin-up or spin-down. [b] In an Ar matrix at 10 K, from ref 34. Note that large regions of the spectrum are obscured by strong Rh-atom absorptions.

The symmetric combination of the two H_2O σ lone pair orbitals interacts with the Rh–Rh σ orbitals ($4a_{1g}$ and $5a_{1g}$); the antisymmetric combination interacts with the Rh–Rh σ^* orbitals ($3a_{2u}$ and unoccupied $4a_{2u}$). The two original $Rh_2(O_2CH)_4$ orbitals, and the three of $Rh_2(O_2CH)_4(H_2O)_2$ which result, are depicted for both cases in Figures 3 and 4. The lowest of the three, most like the H_2O lone pairs, are Rh–OH_2 bonding; the highest, the main Rh–Rh σ and σ^* orbitals, are Rh–Oh_2 antibonding; the middle pair are mainly formate and hence approximately Rh–OH_2 nonbonding. The point is that metal–*metal* bonding weakens both of the metal–*water* interactions. In a_{1g} symmetry, it stabilizes the Rh–Rh σ orbital so that it becomes fully occupied. Thus both the bonding and antibonding Rh–OH_2 a_g orbitals end up filled, and little, if any, net bonding results. Similarly, in a_{2u} symmetry, Rh–Rh bonding destabilizes the Rh–Rh σ^* orbital, so that it is further away in energy, and thus interacts more weakly, with the water lone pairs than it would if the Rh–Rh bond were absent. Thus we can see both why the metal–water bond is weaker than normal, and why bonds to trans ligands get weaker as the metal–metal bond gets stronger: the stronger the metal–metal bond, the higher in energy the σ^* orbital will be. The extremely long Mo–N distance of 2.55 Å in $Mo_2(O_2CCF_3)_4(py)_2$ is thus seen as a necessary consequence of the very strong Mo–Mo σ bond (see Figure 2).

This orbital picture of the trans influence emphasizes its mutual nature: ligands trans to the metal–metal bond will always be more weakly bound than normal, but they in turn will always weaken the metal–metal bond somewhat. As Figure 3 shows, the net effect of the H_2O molecules on the Rh–Rh σ orbitals is a small shift of Rh–Rh bonding electrons to higher energy, corresponding to a weakening of the Rh–Rh bond. The effect is not as dramatic as Figure 1 might indicate, since only the *most important* Rh–Rh σ orbitals are connected there. More significant for the Rh–Rh bond weakening, and not clear from Figure 1, is the influence of H_2O on the Rh–Rh σ^* system. Figure 4 shows that, in contrast to the σ system, the upper two b_{1u} orbitals of $Rh_2(O_2CH)_4(H_2O)_2$ correlate very directly with the original two a_{2u} orbitals of $Rh_2(O_2CH)_4$. The presence of the "extra" $4b_{1u}$ orbital in the hydrate thus corresponds to a shift of Rh–Rh antibonding electrons to lower energy. It should be kept in mind that our calculated difference in Rh–Rh bond strength between $Rh_2(O_2CH)_4$ and $Rh_2(O_2CH)_4(H_2O)_2$ represents a lower limit, since we have kept the Rh–Rh distance in the former at the experimental value for the latter, 2.39 Å.

Experimental facts confirm the competitive nature of metal–metal and metal–trans ligand bonds. In $Rh_2(O_2CCH_3)_4(PPh_3)_2$, the Rh–P bonds of 2.48 Å are ca. 0.15 Å longer than normal.[25] This lengthening is not as great as for the Rh–OH_2 bonds in the hydrate (ca. 0.27 Å[19]); PPh_3 is apparently better than H_2O at competing with the other Rh atom as a ligand. Consequently, the Rh–Rh bond is 0.06 Å longer than in the hydrate. Similar comparisons[45a] hold for $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCF_3)_4(py)_2$ (see Table I); for $Cr_2(O_2CCH_3)_4$ and $Cr_2(O_2Cch_3)_4(H_2O)_2$;[45b] and for $Re_2Cl_8^{2-}$ and $Re_2Cl_8(H_2O)_2^{2-}$.[45c]

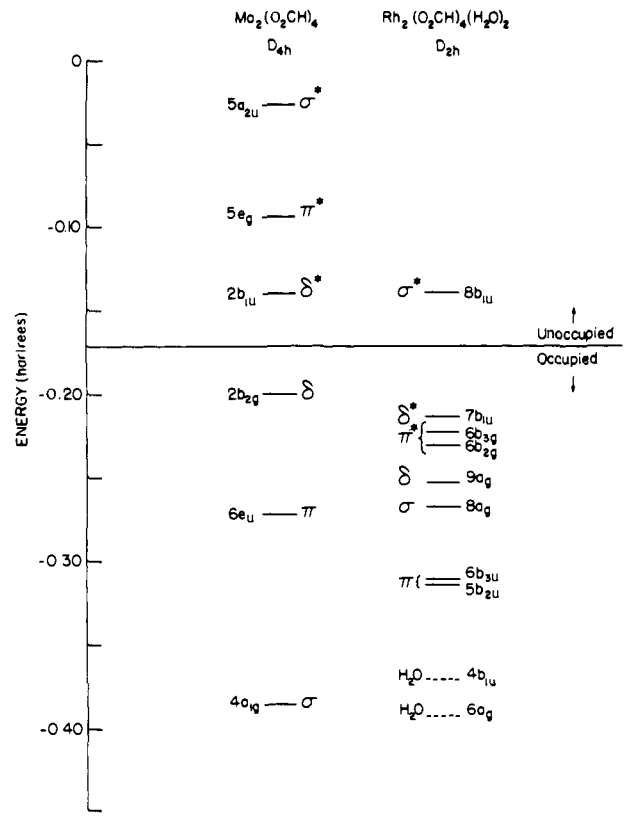


Figure 2. Most important energy levels of $Mo_2(O_2CH)_4$ and $Rh_2(O_2CH)_4(H_2O)_2$ for metal–metal and metal–water bonding. The symbols σ, π, δ, δ^*, π^*, and σ^* refer to metal–*metal* character. For metal–*water* interaction, $6a_g$ and $4b_{1u}$ have σ character, while $8a_g$ and $8b_{1u}$ are σ^*.

$RH_2(O_2CH)_4(H_2O)_2$ and $Mo_2(O_2CH)_4$. The chief difference between the energy levels of these two molecules not already noted is the general downshift of mainly d levels in the Rh case—in contrast to the mainly formate levels, which remain at virtually the same energies. The exception is, of course, the main metal–metal σ orbital, destabilized by the water interaction so that it even lies above the π orbital (see Figure 2).

This downshift is due to the greater electronegativity of Rh than Mo. A consequence is greater ligand character in the ten mainly d orbitals; they average 81% Mo, but only 71% Rh. This does not imply significantly more covalent metal–formate oxygen bonds; the eight M–O *bonding* orbitals are 27% Rh, compared to 25% Mo. The extra attraction of the metal for electrons is thus used almost entirely in binding the two H_2O molecules.

Electronic Spectra of Rh_2^{4+} and Rh_2^{5+} Complexes. The electronic spectrum of rhodium(II) acetate in water consists of two weak bands in the visible region and two stronger bands, the first a shoulder on the second, in the ultraviolet.[27] As the axial water ligands are replaced by stronger donors, band I shifts uniformly to higher energy, while band II remains relatively constant. Bands III and IV shift to lower energies, the former faster than the latter.[22] We have not done transition-state calculations of the spectrum, and so have no absolutely quantitative predictions of transition energies to offer. An entirely reasonable assignment, however, emerges from ground-state energy differences, the magnitudes of relaxation

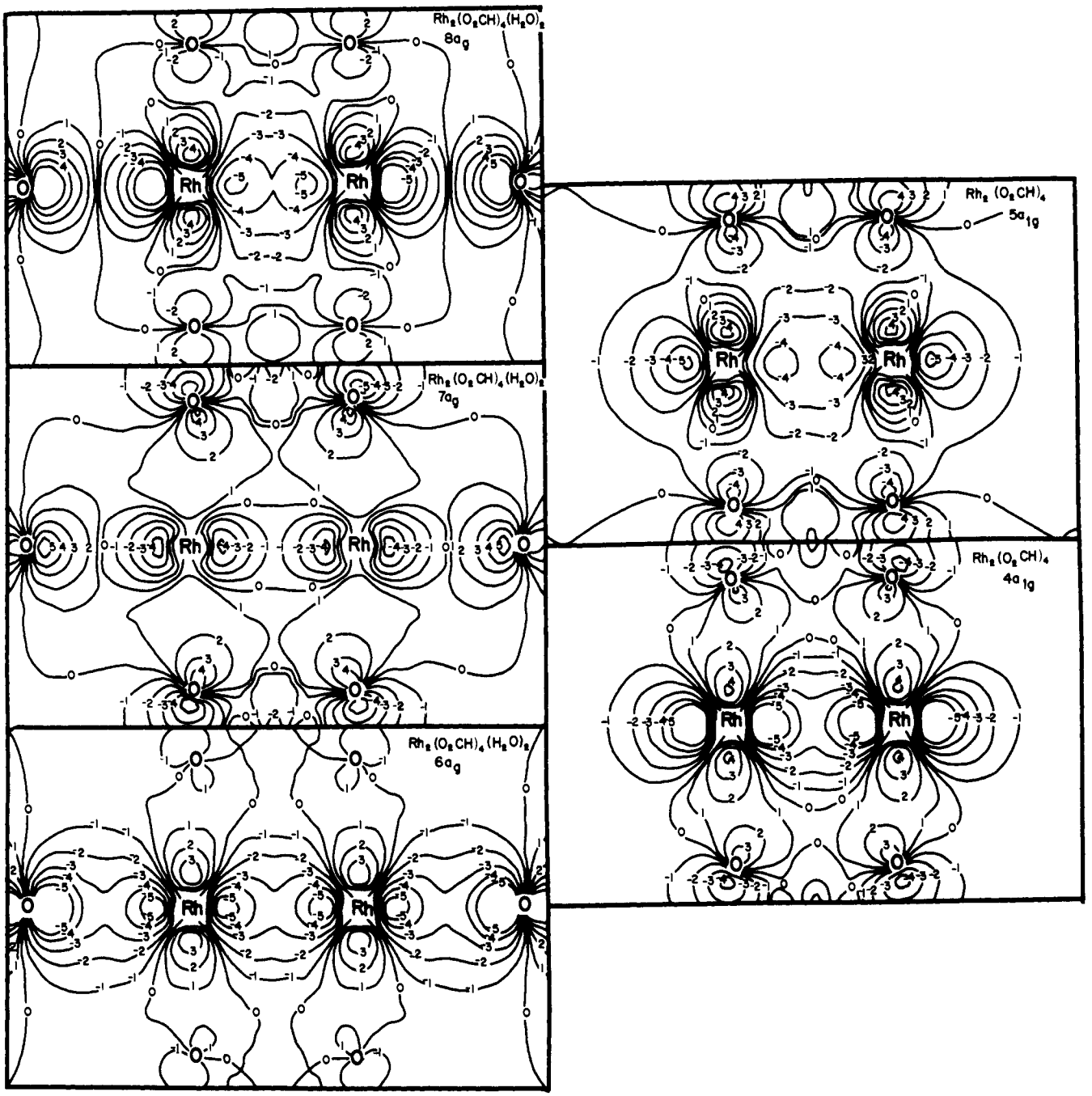


Figure 3. Contour maps of the wave functions for the important Rh–Rh σ levels of $Rh_2(O_2CH)_4(H_2O)_2$ and $Rh_2(O_2CH)_4$, showing the bonding of the trans H_2O molecules in a_g symmetry. These maps and those of Figure 4 are in the plane of two of the formate groups, with contour values of 0, ±1, ±2, ±3, ±4, ±5 = 0, ±0.02, ±0.05, ±0.09, ±0.13, ±0.17, respectively. Interior contours close to the atomic centers are always omitted for clarity.

we expect from experience for various types of transitions, and the above experimental observations; it is given in Table IV. We consider only transitions allowed in D_{4h} symmetry.

The predicted spectrum begins with two distinct transitions, $\pi^* \rightarrow \sigma^*$ and $\pi^* \rightarrow$ Rh-O σ^*. The *ground-state* energy differences are 19.5 and 24.4 × 10^{-3} cm^{-1}, respectively. These are close to the experimental positions of bands I and II, 17.1 and 22.7 × 10^{-3} cm^{-1}, respectively, and we expect little relaxation in the transition state. Moreover, taking the comparison between $Rh_2(O_2CH)_4$ and $Rh_2(O_2CH)_4(H_2O)_2$ in Figure 1 as indicative of changes when the axial-ligand donor strength is increased, we see that $\pi^* \rightarrow \sigma^*$ should go up while $\pi^* \rightarrow$ Rh-O σ^* remains constant. Finally, the essentially d→d character of both transitions suggests that they should be weaker than an ordinary allowed excitation. The complete consistency of these predictions with experiment gives us confidence that we have correctly assigned bands I and II.

Nine allowed transitions have energies fairly close to those of bands III and IV. However, only two of these should show the observed red shift as axial donor strength increases. The reason, again referring to Figure 1, is that only Rh-Rh σ-type orbitals are significantly elevated in energy by the axial donors. For this purpose one should associate $8a_g$ and $7a_g$ in the hydrate with $5a_{1g}$ and $4a_{1g}$ in $Rh_2(O_2CH)_4$, respectively. The only allowed transitions of reasonable energy originating in $8a_g$ and $7a_g$ terminate in $8b_{1u}$, the Rh-Rh σ^* orbital. We thus assign band III to $8a_g \rightarrow 8b_{1u}$ and band IV to $7a_g \rightarrow 8b_{1u}$. As expected from the considerable ligand to metal charge transfer in the predicted transitions, more for the second than the first, the intensities of bands III and IV are greater than for bands I and II, band IV being stronger than band III. The ground-state energy difference for $7a_g \rightarrow 8b_{1u}$, 43.8 × 10^{-3} cm^{-1}, is close

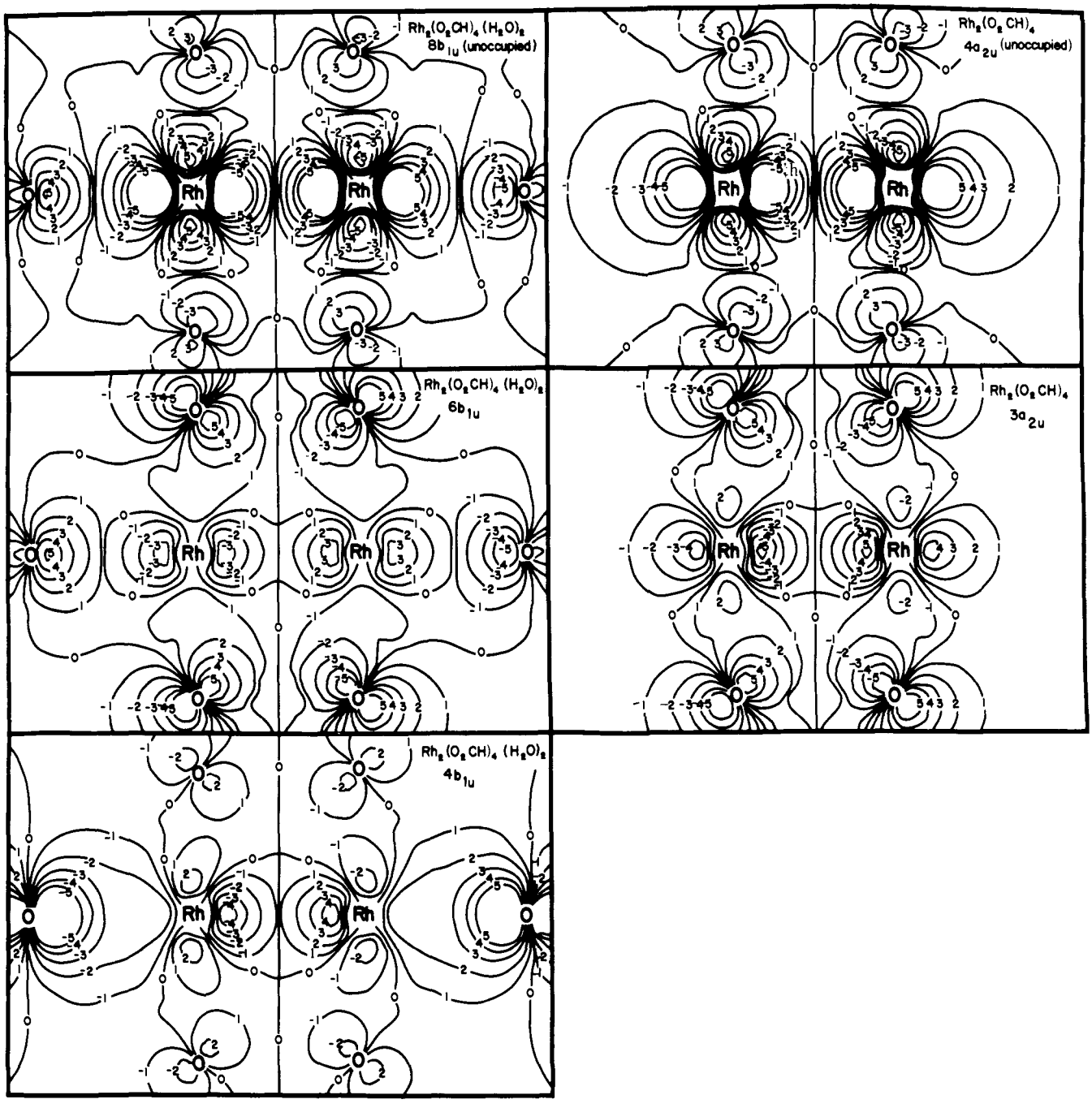


Figure 4. Contour maps of the wave functions for the important Rh-Rh σ^* levels of $Rh_2(O_2CH)_4(H_2O)_2$ and $Rh_2(O_2CH)_4$, showing the bonding of the trans H_2O molecules in b_{1u} symmetry.

the experimental energy of band IV, 45.9×10^{-3} cm^{-1}. The low ground-state value for $8a_g \rightarrow 8b_{1u}$, 29.0 compared to 40 for band III, is not surprising since this is essentially the Rh-Rh $\sigma \rightarrow \sigma^*$ transition, and thus should show very great ground to transition state relaxation.

Our assignment of bands I, II, and III parallels that of Dubicki and Martin based on an extended-Hückel calculation.[22] Their arguments were based more on using the calculation as a rough guide to interpret the spectral changes caused by different axial ligands since, e.g., the extended-Hückel diagram would predict the $\pi^* \rightarrow$Rh-O σ^* transition at lower energy than $\pi^* \rightarrow \sigma^*$. Their assignment of band IV corresponds in our scheme to $6b_{1u} \rightarrow 11a_g$ ($L\sigma^* \rightarrow$Rydberg); we consider this unlikely as our calculated ground-state energy difference is 62.9 $\times 10^{-3}$ cm^{-1}.

The spectra of $Rh_2(CO_3)_4^{4-}$, $Rh_2(SO_4)_4^{4-}$, and $Rh_2(H_2O)_{10}^{4+}$ are so similar to that of rhodium(II) acetate[27] that we propose an entirely analogous assignment, and a similar electronic structure in general, for them. Noteworthy is the downshift of the metal-metal bands for $Rh_2(H_2O)_{10}^{4+}$ relative to the acetate, as expected if the Rh-Rh bond has lengthened upon replacing bridging acetate with nonbridging water ligands.

The solution spectrum of the ephemeral ion $[Rh_2(O_2CCH_3)_4]^+$ also closely resembles that of the neutral species, with the addition of a new low-energy band at 12.3×10^{-3} cm^{-1} (ϵ 476).[27,46] We tentatively suggest that this is the $\delta \rightarrow \delta^*$ transition ($9a_g \rightarrow 7b_{1u}$), made possible by the removal of one δ^* electron upon ionization. Another possibility is $7b_{2,3u} \rightarrow 6b_{2,3g}(\pi \rightarrow \pi^*)$, if π^* rather than δ^* is the HOMO. Our spin-restricted transition-state calculations give ionization energies of 8.23 and 8.41 eV for the $7b_{1u}(\delta^*)$ and $6b_{3g}(\pi^*)$

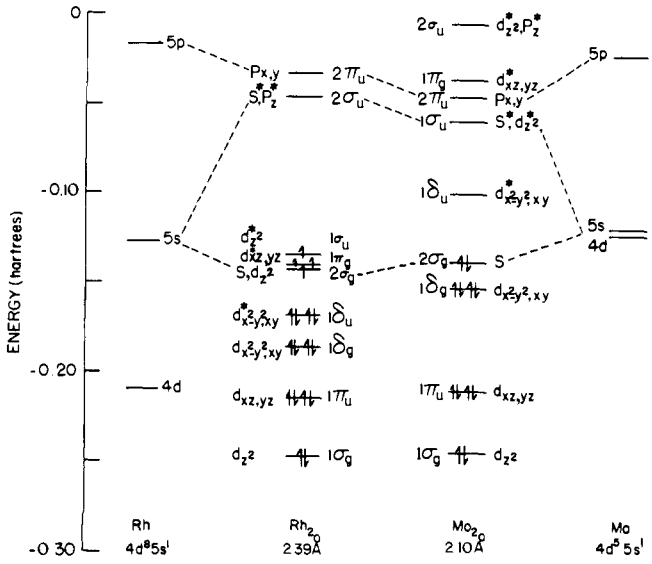


Figure 5. Spin-restricted valence energy levels for Rh_2, Mo_2, Rh, and Mo. Analogous spin-polarized levels for Rh_2 exhibit spin-spin splittings averaging 0.043 hartree, the $1\sigma_g\uparrow$ level being at −0.264 hartree. Levels of Rh_2 and Mo_2 which best correlate with 5s and 5p atomic orbitals are connected by dashed lines; all other levels best correlate with 4d orbitals. $d_{xz,yz}$ refers to a degenerate bonding combination of d_{xz} or d_{yz} orbitals, d_{z^2}* to a nondegenerate antibonding combination of d_{z^2} orbitals, etc.

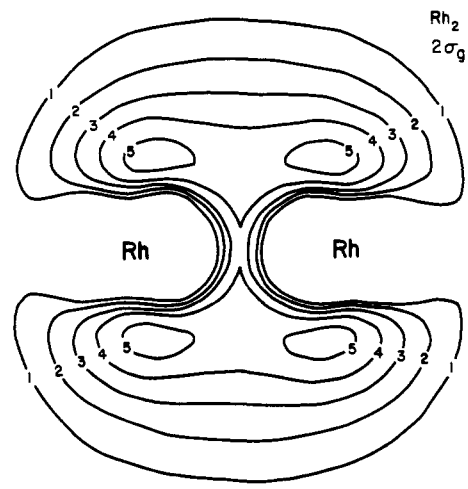


Figure 6. Contour map of the wave function for the $2\sigma_g$ level of Rh_2 at Rh-Rh = 2.39 Å. The contour values are 0, 1, 2, 3, 4, 5 = 0, 0.02, 0.03, 0.04, 0.05, 0.06, respectively.

orbitals, respectively, of $Rh_2(O_2CH)_4(H_2O)_2$, thus predicting that δ* remains highest in the positive ion. We do not consider that we can very firmly predict the HOMO for either neutral acetate or its ion, however, in view of the close spacing, previous difficulty in accurately defining the δ* position,[3a] and possible small differences between the formate and acetate.

Rh_2 and Mo_2. The recent measurements of electronic spectra and other properties for transition-metal diatomics such as Sc_2,[47] Ti_2,[47] V_2,[48] Nb_2,[49] Cr_2,[36,50] Mo_2,[36,49] CrMo,[36] Ni_2,[51] and Rh_2[34] in Ar matrices at low temperature provide experimental access to the interesting and fundamental phenomenon of strong bonds between two metal atoms in the complete absence of ligands. We have previously presented some SCF-Xα-SW results for Cr_2, CrMo, and Mo_2, including a very successful assignment of their measured electronic spectra.[3a,36] Here we briefly compare our initial ground-state calculations on Rh_2 with those on Mo_2.

The "$d^{10}s^2$" valence configuration found for Mo_2 is just a doubling of the d^5s^1 configuration of the atom. In contrast, as shown in Figure 5, dimerization of Rh apparently leads to replacement of one s by one d electron; the configuration is "$d^{17}s^1$". This is a result of the smaller d-band splitting in Rh_2 (that for Mo_2 is still about 50% greater even if Mo-Mo = 2.39 Å is used), and the downshift of 4d relative to 5s orbitals, which leaves the s-type $2\sigma_g$ and d-type $1\pi_g$ and $1\sigma_u$ in such proximity as to favor an open-shell $S = 2$ ground state. Despite the contraction of the d orbitals, the net bonding is still largely d in character.[52] Naive subtraction of antibonding from bonding electrons leaves a net bond order of two, compared to six in Mo_2. Comparison of Figure 6 with its counterpart (Figure 7) in ref 3a shows the effect of the ca. 10% d_{z^2} character which the mainly s orbital has acquired in Rh_2. It remains, however, much more diffuse than the d-like orbitals; note the smaller contours required for good resolution than in Figures 3 and 4.

These conclusions are likely to remain valid for a fair range of Rh-Rh distances around 2.39 Å. As yet we have neither an experimental nor theoretical estimate of the actual bond distance. The former is unlikely to appear in the near future; we intend to investigate the latter problem through calculations at several bond distances, using the Xα-SW total energy and comparisons of the calculated and experimental electronic spectrum as guides. As shown in Table V, the 2.39 Å calculation of the spectrum does not yield a clear assignment. Qualitative consideration of how the predicted transition energies would change with distance does, however, suggest that such an assignment may emerge from the transitions listed in Table V at some other distance. Whether this will actually occur, and whether at a large or smaller distance, remains to be seen.

Ru(2.5) Carboxylates. Dinuclear ruthenium carboxylates are unique among this class of compounds in being stable as positive ions and highly paramagnetic (three unpaired electrons).[53] $[Ru_2(O_2CC_3H_7)_4]Cl$ exhibits Ru-Ru = 2.28 Å,[17] intermediate between the metal-metal distances of 2.09 and 2.39 Å in molybdenum(II) and rhodium(II) carboxylates. We recall that the basic electronic structure of $Rh_2(O_2CH)_4(H_2O)_2$ is generated merely by adding six electrons to the Xα-SW diagram for $Mo_2(O_2CH)_4$ (see Figure 2). This suggests that the ground state of $[Ru_2(O_2CR)_4]Cl$ is $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$, the open-shell character resulting from close spacing of the π* and δ* orbitals.[54] Our Xα-SW calculations on $[Ru_2(O_2CH)_4]Cl$ have proceeded far enough to explicitly confirm this suggestion. Details will appear in a latter publication.[55]

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Crystal and Molecular Structure of a Covalent Perchloric Acid Ester: *p*-Tolylsulfonylmethyl Perchlorate

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Abstract: The crystal and molecular structure of *p*-tolylsulfonylmethyl perchlorate (**2a**) has been analyzed by x-ray diffraction methods. The crystals are monoclinic, the space group is $P2_1/c$; $a = 11.796$ (3), $b = 5.242$ (2), $c = 20.320$ (5) Å, $\beta = 114.28$ (2)°. The structure has been refined to an R factor of 0.072 on 1723 reflections with $|F_o| > 3\sigma_c(F_o)$. The bond lengths and angles around the central methylene carbon (C(8)) unequivocally demonstrate the covalent bonding between C(8) and O(3) of the perchlorate group. Important molecular parameters are as follows: C(8)–S(1) = 1.805 (4), C(8)–O(3) = 1.423 (5), Cl(1)–O(3) = 1.641 (4), Cl(1)–O(4) = 1.397 (5), Cl(1)–O(5) = 1.379 (5), and Cl(1)–O(6) = 1.407 (6) Å. The reduced π character of the Cl(1)–O(3) bond is reflected in the marked increase in bond length relative to the other Cl(1)–O bonds. Short intermolecular C–H···O distances (H(82)···O(2) = 2.184 (3) Å) indicate strong intermolecular hydrogen bonding between the methylene protons and a sulfonyl oxygen atom of an adjacent molecule.

Ever since the preparation of ethyl perchlorate (**1**) by Hare and Boye[1] in 1841, it has been recognized that most neat perchlorate esters, in which the ClO_4 function is covalently bound to carbon, are extremely hazardous compounds, being sensitive to heat, shock, and friction.[2] Their strong explosive violence has not encouraged structural[3] and chemical investigation[4,5] despite the obvious theoretical interest[6] and easy synthetic accessibility[7] of these types of compounds.

Recently, crystalline and relatively stable alkyl- and arylsulfonylmethyl perchlorates (**2**) were prepared from the reaction of α-diazosulfones with perchloric acid.[8]

$CH_3CH_2OClO_3$	$RSO_2CH_2OClO_3$
1	**2**
	a, R = *p*-$CH_3C_6H_4$

Employing appropriate safety precautions, handling of small (ca. 0.1 g) quantities of these compounds involves little hazard

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