Electronic Structure of Rhodium(II) Dimers of Formula $[Rh_2X_2(\mu\text{-}O_2CH)_2(HN{=}CHCH{=}NH)_2]$ (X = halide)†

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The electronic structures of the dirhodium complexes $[Rh_2(\mu\text{-}O_2CH)_4(H_2O)_2]$ and $[Rh_2X_2(\mu\text{-}O_2CH)_2(HN{=}CHCH{=}NH)_2]$ (X = Cl, Br or I) have been calculated by the Fenske–Hall method. The calculations gave the electronic configurations $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^*$ with σ^* as the lowest unoccupied molecular orbital for $[Rh_2(\mu\text{-}O_2CH)_4(H_2O)_2]$ and highest occupied molecular orbital $< 18a_1$, $16b_1$ (π^* HN=CHCH=NH) $<$ $17b_1$ (σ^*) for $[Rh_2X_2(\mu\text{-}O_2CH)_2(HN{=}CHCH{=}NH)_2]$. All Rh–Rh orbitals of the latter complexes have considerably higher ligand contributions than those of $[Rh_2(O_2CH)_4(H_2O)_2]$. The strength of the Rh–Rh bond and the electronic spectra of the complexes are discussed.

There is considerable interest in metal cluster chemistry and the bimetallic carboxylate complexes are among the most extensively studied cluster compounds. The electronic structure and reactivity of dirhodium(II) tetracarboxylates $[Rh_2(O_2CR)_4L_2]$ (R = alkyl or aryl, L = Lewis base) have been the subject of growing interest in recent years. The nature of the metal–metal interaction in $[Rh_2(O_2CR)_4]$ as well as their adducts has been a source of controversy for years.[1–3]

The Rh–Rh bond in all rhodium(II) dimers is now assumed to be single, although the distance between the rhodium atoms was found to vary within very broad limits.[1–3] This was confirmed by extended-Hückel,[4] SCF-X_α-SW[5] and *ab initio*[6,7] calculations, which gave $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$, $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ and $\pi^2\delta^2\pi^{*4}\delta^{*2}\sigma^2$ electronic configurations. The first of these configurations was confirmed by the ESR spectrum of $[Rh_2(O_2CMe)_4(H_2O)_2]^+$ in aqueous solution[8] and by the electronic spectrum of $[Rh_2\{O_2CCH(OH)Ph\}_4(EtOH)_2]$.[9] The electronic configuration was found to be strongly dependent on the nature of the axial ligands L (Fig. 1). The rhodium(II) carboxylates are effective catalysts for reduction of olefins and for oxidation of alkylarenes. They also catalyse the reactions of diazo compounds with alkenes to produce cyclopropane derivatives.

The majority of rhodium(II) complexes contain bridging ligands, most frequently carboxylates, *i.e.* $[Rh_2(\mu\text{-}O_2CR)_4L_2]$. Compounds containing either fewer bridges, *e.g.* $[Rh_2(O_2CMe)_3(py)_4][CF_3SO_3]$ (py = pyridine),[1–3] $[Rh_2X_2(O_2CR)_2(L\text{–}L)_2]$ [L–L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen); X = Cl, Br or I; R = H, Me or PhCHOH],[10–14] or without bridging ligands, *e.g.* $[Rh_2(Hdmg)_4L_2]$ (H_2dmg = dimethylglyoxime),[1–3] are also known.

The complexes $[Rh_2X_2(\mu\text{-}O_2CR)_2(L\text{–}L)_2]$ are precursors of very active catalysts for hydrogenation of ketones and some show higher cytostatic activity than those of $[Rh_2(O_2CR)_4L_2]$ dimers.[1 3,15,16] Their interesting properties have prompted us to investigate the electronic structure of these compounds and compare it with that of dirhodium(II) tetracarboxylates.

Calculations

Electronic structures of the dirhodium tetra- and di-formato complexes $[Rh_2(O_2CH)_4(H_2O)_2]$ and $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ (X = Cl, Br or I) have been calculated by the semiquantitative Fenske–Hall molecular-orbital method.[17] For all the complexes the basic functions have been constructed using Clementi functions[18] according to the electronic configurations and charges of the atoms. In calculations the following valence basis sets were used: 4d, 5s and 5p atomic orbitals (AOs) of rhodium, ns and np AOs of O, C, N and X (X = Cl, Br or I) and 1s AOs of H. Atomic coordinates for the calculations on $[Rh_2(O_2CH)_4(H_2O)_2]$ were based on its crystal structure[19] and that of $[Rh_2(O_2CMe)_4(H_2O)_2]$[20] (Table 1, Fig. 1). The geometries of the $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ complexes were based on the experimental ones reported for $[Rh_2Cl_2(O_2CH)_2(phen)_2]$[10,13] and $[Rh_2Cl_2(O_2CH)_2(bipy)_2]\cdot 4H_2O$[13,21] (Table 1). The Rh–N distances and the geometries of the HN=CHCH=NH ligands were assumed to be the same as those for bipy and phen ligands in the above-mentioned complexes. The Rh–Br and Rh–I distances were calculated assuming that differences between Rh–X and Rh–Cl distances for $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ complexes are the same as for tetracarboxylato complexes $[Rh_2X_2(O_2CR)_4]^{2-}$ (X = Cl, Br or I). The geometries of the complexes and the coordinate systems used for the calculations are given in Fig. 1.

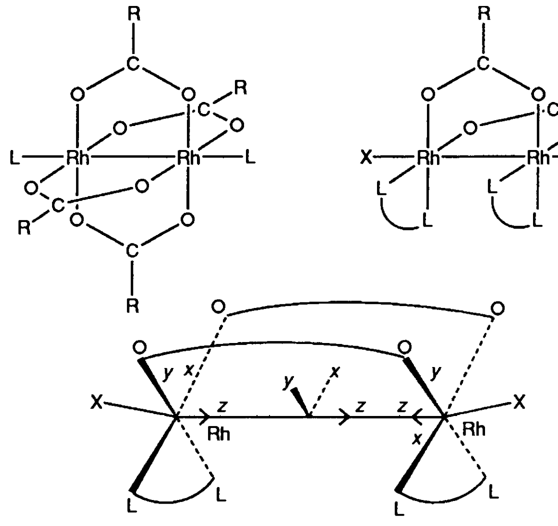

Fig. 1 Structure of $[Rh_2(O_2CR)_4L_2]$ and $[Rh_2X_2(O_2CR)_2(L\text{–}L)_2]$ and coordinate system used for calculations

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† *Non-SI unit employed:* eV ≈ 1.6 × 10^{-19} J.

Results and Discussion

In Fig. 2 the energies of the valence orbitals of $[Rh_2(O_2CH)_4(H_2O)_2]$ and $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ are depicted and in Fig. 3 the interaction of the orbitals of the Rh_2^{4+} unit with those of two halide ligands X in $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ complexes. Numerical

Table 1 Structural data for $[Rh_2(O_2CR)_4L_2]$ and $[Rh_2X_2(O_2CR)_2(L\text{–}L)_2]$ complexes

	Distances/pm				
Compound	Rh–Rh	Rh–O	Rh–N	Rh–L	Ref.
$[Rh_2(O_2CH)_4(H_2O)_2]$	238	203		245	19
$[Rh_2(O_2CMe)_4(H_2O)_2]$	238.56	202.9–204.7		231	20
$[Rh_2(O_2CMe)_4(PPh_3)_2]$	245.05	203.1–205.6		247.71	1
$[Rh_2Cl_2(O_2CH)_2(bipy)_2]\cdot 4H_2O$	257.8	203.9–204.9	207.1–202.7	252.1	13, 21
$[Rh_2Cl_2(O_2CH)_2(phen)_2]$	257.6	206.3–206.9	199.9–201.0	249.6 250.4	13

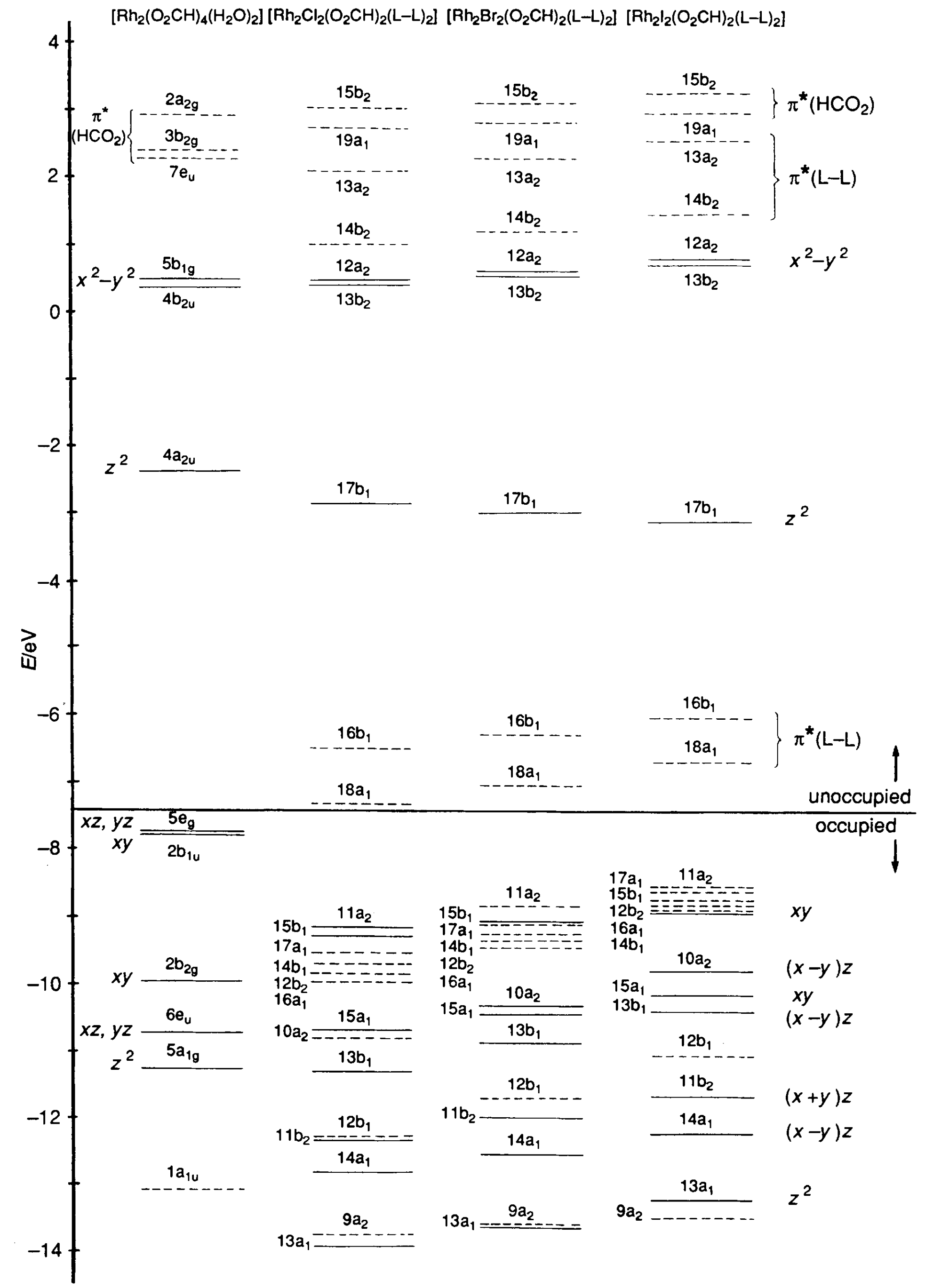

Fig. 2 The most important electronic levels of $[Rh_2(O_2CH)_4(H_2O)_2]$ and $[Rh_2X_2(O_2CH)_2(L\text{–}L)_2]$ (X = Cl, Br or I)

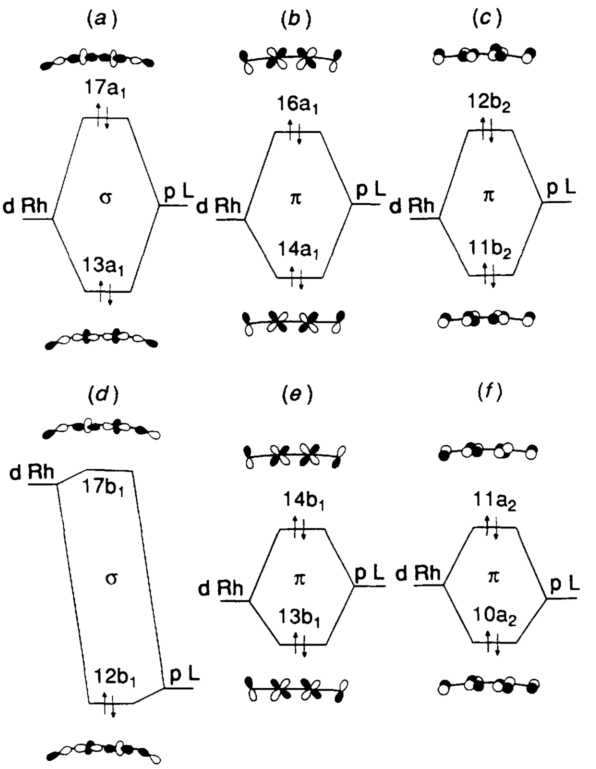

Fig. 3 Diagram of the interaction of orbitals of the Rh_2^{4+} core with halide ligands in $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$

values for these compounds are listed in Table 2. For $[Rh_2(O_2CH)_4(H_2O)_2]$ the calculations gave the electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^*$ with a π^* highest occupied molecular orbital (HOMO) and σ^* lowest unoccupied molecular orbital (LUMO). Thus Fenske–Hall calculations on $[Rh_2(O_2CH)_4(H_2O)_2]$ lead to good agreement with the extended-Hückel[4] and *ab initio* self consistent field-configuration interaction (SCF/CI)[7] methods. Very good agreement was also obtained between Hartree–Fock and Fenske–Hall calculations in the case of vanadium(II) dimers.[22] For $[Rh_2(O_2CH)_4(H_2O)_2]$ the Rh–Rh bonding orbitals are of symmetry $5a_{1g}$, $6e_u$ and $2b_{2g}$, while the antibonding ones are $2b_{1u}$, $5e_g$ and $4a_{2u}$. The bonding orbitals comprise at least 80% Rh and at the same time they are antibonding rhodium–ligand orbitals (Table 2). However, the $4a_{1g}$ and $5e_u$ orbitals, with lower energy, which are both Rh–Rh and rhodium–ligand bonding, comprise a little more than 20% Rh. The water molecules co-ordinated along the Rh–Rh axis do not perturb the strongly tetragonal (D_{4h}) symmetry of the complex (practically they do not remove the degenerate nature of the e_g and e_u orbitals), however owing to their σ-donor properties they destabilize the $5a_{1g}$ orbital, weakening the Rh–Rh σ bond (Table 2). Therefore the energy levels for $[Rh_2(O_2CH)_4(H_2O)_2]$ were assigned using irreducible representations of the D_{4h} point group. Substitution of the HN=CHCH=NH ligands for two formato groups in tetraformatodirhodium(II) leads to the formation of dimeric complexes of rhodium(II) containing only two bridging ligands $[Rh_2X_2(\mu\text{-}O_2CH)_2(HN{=}CHCH{=}NH)_2]$ of C_{2v} symmetry. Lowering of symmetry leads to the splitting of levels $e_u \longrightarrow a_1 + b_2$, $e_g \longrightarrow a_2 + b_1$, and the introduced ligands influence the nature and magnitude of the splitting which consists in a shift of the electron density, in a change in energy of some electronic levels and in the appearance of empty, low-energy antibonding π^* orbitals ($18a_1$ and $16b_1$) for the HN=CHCH=NH ligands. Thus the order of the higher occupied and lower empty orbitals of the complexes is (Table 2, Fig. 2) HOMO < $18a_1$, $16b_1$ (π^* HN=CHCH=NH) < $17b_1$ (σ^*) < $13b_2$ (δ_2) < $12a_2$ (δ_2^*) < π^* (NH=CHCH=NH) < π^* (O_2CH), where $18a_1$ and $16b_1$ are empty π^* orbitals of HN=CHCH=NH with a substantial participation of rhodium orbitals (*ca.* 15%), $17b_1$ is a Rh–Rh σ^* orbital and the $13b_2$ (δ_2) and $12a_2$ (δ_2^*) Rh–Rh orbitals are Rh–O_2CH and Rh_2–(HN=CHCH=NH) σ^* antibonding and perpendicular to the Rh–Rh axis.

All σ, π, δ, σ*, π* and δ* orbitals of the $[Rh_2X_2(O_2CH)_2(NH{=}CHCH{=}NH)_2]$ complexes contain considerably higher contributions from ligand orbitals than do the corresponding Rh–Rh levels of $[Rh_2(O_2CH)_4(H_2O)_2]$. Particularly large differences are observed for σ, π, σ* and π* orbitals. This is connected with interaction of the orbitals of the Rh_2 core both with HN=CHCH=NH groups and ligands lying along the Rh–Rh axis (Cl, Br, I), *e.g.* in the $14a_1$ (π) and $11b_2$ (π) orbitals of $[Rh_2Cl_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ there is 55 and 72% rhodium contribution while in the $6e_u$ (π) orbitals of $[Rh_2(O_2CH)_4(H_2O)_2]$ this increases to 82%. In the case of the $13b_1$ (π*) and $11a_2$ (π*) orbitals which correspond to the $5e_g$ (π*) orbitals of $[Rh_2(O_2CH)_4(H_2O)_2]$ the delocalization is still higher (Table 2). Of course, these changes influence the nature and strength of the Rh–Rh bond.

The higher valence orbitals are 4d rhodium combinations which interact also with p orbitals of halides co-ordinated along the Rh–Rh bond. In Fig. 2 for clarity only levels with substantial participation of 4d rhodium orbitals are given. The energy of these levels strongly depends on overlapping of d orbitals of the Rh_2^{4+} core and p orbitals of halide ligands and π* orbitals of HN=CHCH=NH groups. For example, the $13a_1$ (σ) level is situated below that of $5a_{1g}$ (σ).

The energy difference between the $17b_1$ (σ*) antibonding and $13a_1$ (σ) bonding levels in $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ complexes is greater than the difference between the $4a_{2u}$ (σ*) and $5a_{1g}$ (σ) orbitals in $[Rh_2(O_2CH)_4(H_2O)_2]$ (Fig. 2, Table 2). This results mainly from the stabilization of $13a_1$ (σ) levels by p_σ orbitals of Cl, Br or I. The effect increases in the order I < Br < Cl.

However, this interaction does not strengthen the σ Rh–Rh bond because in the same order the participation of σ orbitals of the Rh_2^{4+} unit in the $13a_1$ (σ) levels is markedly decreased (almost a factor of 2) compared with the $5a_{1g}$ (σ) level in $[Rh_2(O_2CH)_4(H_2O)_2]$ (Table 1). Simultaneously, substantial contributions (20–33%, Table 2) from σ Rh–Rh orbitals to the antibonding $17a_1$ (σ*) Rh–X levels were found. All these interactions lead to weakening of the Rh–Rh bond due to the *trans* effect of X ligands (Cl, Br or I) occupying axial co-ordination sites. On the other hand the relatively strong σ Rh–Rh bond is associated with the high energy of the $17b_1$ (σ*) Rh–Rh orbital. As a consequence, the interaction of this orbital with p_σ orbitals of axial ligands is weak [Fig. 3(*d*)] and therefore the Rh–X bond is also weak.[5] In the $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ complexes the $12b_1$ orbital is Rh–X bonding. The calculations indicate that participation of Rh in $12b_1$ increases in the order Cl < Br < I and is consistent with the decrease in electronegativity of the halides in the same direction. This suggests that the σ Rh–Cl bond is the weakest, owing to the *trans* effect of the σ Rh–Rh bond. This was confirmed experimentally for $[Rh_2X_2(O_2CR)_2(L\text{–}L)_2]$ complexes (L–L = bipy or phen; X = Cl, Br or I). In water and alcoholic solutions the substitution of solvent (solv) molecules for X ligands takes place most easily in the case of the chloro complex. The equilibrium constant for reaction (1) decreases in the order Cl > Br > I.[12]

$$[Rh_2X_2(O_2CR)_2(L\text{–}L)_2] + n\text{solv} \longrightarrow [Rh_2X_{2-n}(O_2CR)_2(L\text{–}L)_2(\text{solv})_n]^{n+} + nX^- \quad (1)$$

The $14a_1$ (π) and $13b_1$ (π*) orbitals corresponding to the $6e_u$ (π) and $5e_g$ (π*) levels of tetragonal $[Rh_2(O_2CR)_4(H_2O)_2]$ are stabilized owing to their interaction with empty $18a_1$ and

Table 2 Energies (eV) of higher electronic levels and charge distributions for $[Rh_2(O_2CH)_4(H_2O)_2]$ and $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ (X = Cl, Br or I)

		% Charge				
Symmetry	Energy	Rh	O_2CH	L–L	X	Bond type
$[Rh_2Cl_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$						
$13a_1$	−13.96	56	23	5	16	σ Rh_2
$9a_2$	−13.73	—	100	—	—	
$14a_1$	−12.84	55	26	10	9	π Rh_2
$11b_2$	−12.33	72	7	11	10	π Rh_2
$12b_1$	−12.32	29	5	5	61	
$13b_1$	−11.29	46	11	12	31	π* Rh_2
$10a_2$	−10.81	36	5	4	55	
$15a_1$	−10.68	76	4	18	2	δ Rh_2
$16a_1$	−9.97	4	—	6	90	
$12b_2$	−9.85	10	—	—	90	
$14b_1$	−9.69	16	2	11	71	
$17a_1$	−9.53	38	—	12	50	
$15b_1$	−9.33	69	19	10	2	δ* Rh_2
$11a_2$	−9.16	50	3	3	44	π* Rh_2 HOMO
$18a_1$	−7.33	17	1	68	14	π* (L–L) LUMO
$16b_1$	−6.51	24	1	73	2	π* (L–L)
$17b_1$	−2.85	64	6	3	27	σ* Rh_2
$13b_2$	0.41	62	20	18	—	δ* Rh_2
$12a_2$	0.47	64	18	18	—	δ* Rh_2
$[Rh_2Br_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$						
$13a_1$	−13.64	63	17	6	14	σ Rh_2
$9a_2$	−13.61	—	100	—	—	
$14a_1$	−12.54	59	24	10	7	π Rh_2
$11b_2$	−12.00	76	7	11	6	π Rh_2
$12b_1$	−11.71	34	3	8	55	
$13b_1$	−10.86	50	13	12	25	π* Rh_2
$15a_1$	−10.43	76	4	18	2	δ Rh_2
$10a_2$	−10.31	47	5	5	43	π* Rh_2
$16a_1$	−9.45	6	—	9	85	
$12b_2$	−9.34	6	—	—	94	
$14b_1$	−9.26	19	4	7	70	
$17a_1$	−9.10	31	—	14	55	
$15b_1$	−9.10	61	14	11	14	δ* Rh_2
$11a_2$	−8.86	40	2	1	57	π* Rh_2 HOMO
$18a_1$	−7.03	16	1	64	19	π* (L–L) LUMO
$16b_1$	−6.29	24	1	72	3	π* (L–L)
$17b_1$	−2.97	61	5	3	31	σ* Rh_2
$13b_2$	0.56	63	20	17	—	δ* Rh_2
$12a_2$	0.63	64	18	18	—	δ* Rh_2
$[Rh_2I_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$						
$9a_2$	−13.49	—	100	—	—	
$13a_1$	−13.23	69	11	6	14	σ Rh_2
$14a_1$	−12.22	63	21	11	5	π Rh_2
$11b_2$	−11.67	80	5	12	3	π Rh_2
$12b_1$	−11.05	45	1	14	40	
$13b_1$	−10.38	51	12	8	29	π* Rh_2
$15a_1$	−10.16	78	4	17	1	δ Rh_2
$10a_2$	−9.80	59	6	6	29	π* Rh_2
$14b_1$	−8.92	64	16	8	12	δ* Rh_2
$16a_1$	−8.92	5	—	11	84	
$12b_2$	−8.82	4	—	—	96	
$15b_1$	−8.74	14	2	6	78	
$17a_1$	−8.63	25	—	14	61	
$11a_2$	−8.54	27	1	1	71	π* Rh_2 HOMO
$18a_1$	−6.71	15	1	60	24	π* (L–L) LUMO
$16b_1$	−6.04	24	1	72	3	π* (L–L)
$17b_1$	−3.12	58	5	3	34	σ* Rh_2
$13b_2$	0.73	63	20	17	—	δ* Rh_2
$12a_2$	0.80	65	17	18	—	δ* Rh_2

		% Charge			
Symmetry	Energy	Rh	O_2CH	H_2O	Bond type
$[Rh_2(O_2CH)_2(H_2O)_2]$					
$1a_{1u}$	−13.10	—	100	—	
$5a_{1g}$	−11.25	77	17	6	σ Rh_2
$6e_u$	−10.73	82	18	—	π Rh_2
$2b_{2g}$	−9.96	92	8	—	δ Rh_2
$2b_{1u}$	−7.80	75	25	—	δ* Rh_2
$5e_g$	−7.76	91	9	—	π* Rh_2 HOMO
$4a_{2u}$	−2.39	83	11	6	σ* Rh_2 LUMO
$4b_{2u}$	0.36	69	31	—	δ* Rh_2
$5b_{1g}$	0.48	64	36	—	δ* Rh_2
$7e_u$	2.26	1	99	—	
$3b_{2g}$	2.41	3	97	—	
$2a_{2g}$	2.94	—	100	—	

Table 3 Electronic spectra of $[Rh_2(O_2CR)_4L_2]$ and $[Rh_2X_2(O_2CR)_2(L\text{–}L)_2]$ (L = PPh_3, EtOH, py or $NHBu_2$; X = Cl, Br or I; L–L = bipy or phen) in ethanolic and methanolic solutions

Complex	$\lambda/\mu m^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)
$[Rh_2\{O_2CCH(OH)Ph\}_4(PPh_3)_2]$	2.12 (sh),[a] 2.65 (25 200),[b] 3.17 (11 100), 3.67 (sh), 3.87 (sh), 3.97 (sh) (19 000)
$[Rh_2\{O_2CCH(OH)Ph\}_4(py)_2]$	1.84 (260),[a] 2.19 (120),[c] 3.22 (sh) (3 100), 3.68 (sh), 3.80 (11 900), 3.89 (12 600), 4.00 (13 200), 4.13 (14 000), 4.31 (sh) (12 800)
$[Rh_2\{O_2CCH(OH)Ph\}_4(NHBu_2)_2]$	1.74 (200),[a] 2.25 (115),[c] 3.66 (sh) (6 400), 3.79 (6 900), 3.88
$[Rh_2\{O_2CCH(OH)Ph\}_4(EtOH)_2]$	1.70 (240),[a] 2.22 (120),[c] 2.44 (sh) (80), 3.00 (sh), 3.80 (sh) (4 300), 3.89 (5 100), 3.98 (5 200), 4.31 (10 300)
$[Rh_2Cl\{O_2CCH(OH)Ph\}_2(bipy)_2(EtOH)]^+$	1.80 (400),[a] 2.30 (3 000),[d] 2.65 (5 300), 3.23 (sh), 3.66 (39 400)[b]
$[Rh_2Br\{O_2CCH(OH)Ph\}_2(bipy)_2(MeOH)]^+$	1.80 (330),[a] 2.33 (3 300),[d] 2.60 (sh) (5 500), 3.03 (sh) (16 600), 3.24 (21 900),[b] 3.66 (32 000)
$[Rh_2I\{O_2CH(OH)Ph\}_2(bipy)_2(MeOH)_2]^+$	1.83 (sh) (750),[a] 2.21 (sh) (6 700),[d] 2.50 (14 400),[b] 2.79 (13 400),[b] 3.25 (sh) (12 600), 3.58 (23 000), 3.79 (sh) (20 700), 3.86 (sh) (19 800)

[a] π^* $(Rh_2) \longrightarrow \sigma^*$ (Rh_2). [b] σ (Rh–L) $\longrightarrow \sigma^*$ (Rh_2). [c] π^* $(Rh_2) \longrightarrow \sigma^*$ (Rh–O), σ^* (Rh–N). [d] σ $(Rh_2) \longrightarrow \pi^*$ (bipy).

$16b_1$ orbitals of HN=CHCH=NH molecules. Additionally these orbitals and the $11b_2$ (π) orbital [corresponding to $6e_u$ (π) of the tetrahedral complex] are lowered in energy due to the interaction with p_π orbitals of Cl, Br or I [Fig. 3(*b*), 3(*c*), 3(*e*)]. The remaining a_2 orbital, obtained from $5e_g$ (π^*) orbitals by lowering of symmetry ($C_{4h} \longrightarrow C_{2v}$), interacting with p_π orbitals of axial ligands [Fig. 3(*f*)] gives $10a_2$ (π^*) and $11a_2$ (π^*) orbitals strongly delocalized in the Rh–X bond. For the chloro complex, owing to the higher electronegativity of chlorine, the $11a_2$ (π^*) orbital has Rh_2^{4+} character, while in the bromo and iodo complexes $10a_2$ (π^*) plays the role of a Rh_2^{4+} orbital.

Electronic Spectra of $[Rh_2X_2(O_2CR)_2(L\text{–}L)_2]$ *Complexes.*—Calculations were carried out for complexes with HN=CHCH=NH. However, 1,10-phenanthroline and 2,2′-bipyridine have the same skeleton of atoms interacting with the rhodium atoms. Thus it can be assumed that the energy levels for $[Rh_2X_2(O_2CR)_2(phen)_2]$ and $[Rh_2X_2(O_2CR)_2(bipy)_2]$ are similar to those for $[Rh_2X_2(O_2CR)_2(HN{=}CHCH{=}NH)_2]$, and that at approximately the same energy should appear empty π^* orbitals of phen and bipy with mainly p character from N and C atoms and relatively strong d_π character from the Rh_2 core. The influence of the O_2CR ligands on the electronic structure of these complexes is not very different from the effect of a O_2CH group. This follows from similarity of the electronic spectra of $[Rh_2X_2(O_2CR)_2(L\text{–}L)_2]$ complexes (R = H, Me, PhCHOH or MeCHOH; L–L = bipy or phen; X = Cl, Br or I).[3,10,12] Therefore it should be possible to use the results of these calculations to explain the electronic spectra of $[Rh_2X_2(O_2CR)_2(phen)_2]$ and $[Rh_2X_2(O_2CR)_2(bipy)_2]$ complexes.

In the electronic spectra (Table 3) of these complexes in the visible region two bands are observed. Band I occurs at about 1.8–1.83 μm^{-1}, about 0.1 μm^{-1} higher compared with that for $[Rh_2(O_2CR)_4(H_2O)_2]$ compounds. This shift may be explained by assuming that band I corresponds to the π^* $(Rh_2) \longrightarrow \sigma^*$ (Rh_2) transition (Table 2, Fig. 2), since the π^* (Rh_2) ($11a_2$ and $14b_1$) levels in $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ complexes have lower energy than that of the $5e_g$ orbitals in $[Rh_2(O_2CH)_4(H_2O)_2]$. The decrease results from a greater Rh–Rh distance and therefore from weaker π (Rh_2) interaction in complexes with diazabutadienes as compared with $[Rh_2(O_2CH)_4(H_2O)_2]$. However, the position of band I in the spectra of $[Rh_2X_2(O_2CH)_2(HN{=}CHCH{=}NH)_2]$ essentially does not change for different halide ligands. This indicates a weak interaction of the axial halides with the rhodium atoms. The intense band II at about 2.3 μm^{-1} appears only for complexes containing bipy and phen ligands. This band obscures the absorption of low intensity attributed to the π^* $(Rh_2) \longrightarrow \sigma^*$ (Rh–O) transition which corresponds to the transition $5e_g \longrightarrow 4b_{2u}$ of $[Rh_2(O_2CR)_4(H_2O)_2]$ observed at 2.25–2.50 μm^{-1}.

Band II, on the grounds of calculation and its intensity, was assigned to the allowed charge-transfer (c.t.) transition σ $(Rh_2) \longrightarrow \pi^*$ (L–L) ($13a_1 \longrightarrow 18a_1$). In the spectra of bromo and iodo complexes there are additional bands in the regions 3.1–3.3 and 2.5–2.8 μm^{-1}, the high absorption coefficients and relative position of which indicate that they should be assigned to the σ (Rh–X) $\longrightarrow \sigma^*$ (Rh_2) charge-transfer. It is difficult to observe an analogous transition for the chloro complex, expected at 3.6–4.0 μm^{-1}, because in this region there is very intense absorption corresponding to internal transitions in the bipy and phen ligands. These assignments are also supported by the values of the optical electronegativity of Cl^-, Br^- and I^- (3.0, 2.8 and 2.5 respectively) and by the occurrence of P$\longrightarrow$Rh c.t. bands in the spectra of complexes containing phosphine ligands co-ordinated along the Rh–Rh axis [the optical electronegativities of I^- and PR'_3 (X_{opt} = 2.6) are similar]. Such bands are found in the range 2.50–2.80 μm^{-1} in the case of $[Rh_2(O_2CR)_4(PR'_3)_2]$ complexes and in the region 2.31–2.35 μm^{-1} for $[Rh_2X_{2-n}(O_2CR)_2(L\text{–}L)_2(PR'_3)_n]^{n+}$ (R = aryl, R′ = alkyl) compounds.[10,12,21]

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