

## ELECTRONIC STRUCTURE OF DIRHODIUM TETRACARBOXYLATE COMPLEXES BY THE AB INITIO SCF MO METHOD

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Electronic structures of dirhodium tetracarboxylate (DRTC) complexes with ligand (L) free, L = OH<sub>2</sub>, NH<sub>3</sub>, and PH<sub>3</sub> have been calculated by the ab initio SCF MO method with a STO-3G basis set. The Rh–Rh bond is a weak single bond. The electronic configuration is  $\pi^4\delta^2\pi^*4\delta^*2\sigma^2$  for L free, L = OH<sub>2</sub>, and NH<sub>3</sub>, and  $\delta^2\pi^4\pi^*4\delta^*2\sigma^2$  for L = PH<sub>3</sub>. The HOMO is  $\sigma$  for all the complexes, and for L = PH<sub>3</sub>, this is in accord with an ESR experiment.

### 1. Introduction

Dirhodium tetracarboxylate (DRTC) complexes, Rh<sub>2</sub>(O<sub>2</sub>CH)<sub>4</sub>L<sub>2</sub> (fig. 1) have Rh–Rh bond lengths from 2.38 to 2.46 Å [1,2], considerably shorter than those in ordinary dirhodium complexes, 2.7–2.8 Å [3,4]. Cotton and co-workers [4,5] formally attributed this abnormality to a possible triple bond of Rh–Rh with electronic configuration  $\sigma^2\pi^4\delta^2\delta^*2\sigma_n^2\sigma_n'^2$ . Recently, Norman and Kolari [6] reported SCF X $\alpha$  SW calculations for DRTC with L free and L = OH<sub>2</sub> and found the electronic configuration  $\sigma^2\pi^4\delta^2\pi^*4\delta^*2$ , suggesting a single Rh–Rh bond. Their results for corresponding cation radicals [7] have shown the same MO sequence of  $\sigma^2\pi^4\delta^2\pi^*4\delta^*1$ ; the singly occupied orbital was predicted to be of  $\delta^*$  symmetry. A recent ESR study by Kawamura et al. [8] has shown, however, that the singly occupied orbitals of DRTC cat-

ions with phosphorus-centered ligands have  $\sigma$  symmetry and the Rh–Rh bond is essentially single in nature. We report here our preliminary results for the electronic structure of DRTC with L, free, L = OH<sub>2</sub>, NH<sub>3</sub>, and PH<sub>3</sub> obtained by the ab initio Hartree–Fock SCF MO method.

### 2. Electronic structure of DRTC complexes

We have carried out Hartree–Fock SCF MO calculations using a slightly modified version of the HONDO program [9]. The geometries of the DRTC complexes are based on the experimental ones reported by Christoph and Koh [1]; the (Rh–Rh, Rh–L) lengths (in Å) are (2.39, –), (2.39, 2.310), (2.403, 2.308), and (2.449, 2.479) for L free, L = OH<sub>2</sub>, NH<sub>3</sub>, and PH<sub>3</sub>, respectively. For ligand free DRTC, the Rh–Rh length was varied with the remaining geometry fixed. The basis set is at the minimal STO-3G level [10]. For rhodium we have considered the inner shell, 4d, 5s, and 5p AOs † with the Slater exponents reported by Clementi et al. [11]. For phosphorus, we examined the effect of outer 3d orbitals. For the 3d orbital we used a single gaussian orbital with  $\zeta = 0.015$  or 0.43 [12]. The former is the exponent for a Rydberg 3d or-

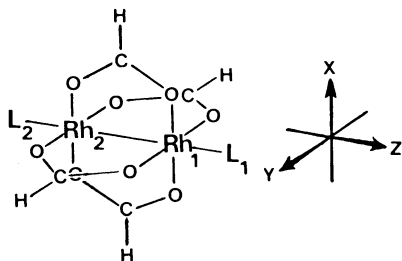


Fig. 1. Geometry of dirhodium tetracarboxylate complexes.

† For the 5p AO we have assumed the same exponent as that of the 5s AO.

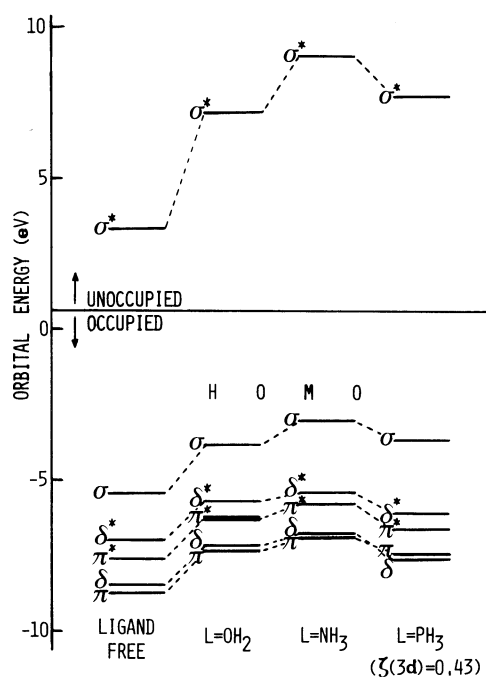


Fig. 2. Orbital energy level diagram for the MOs pertinent to the Rh–Rh bond in dirhodium tetracarboxylate complexes.

bital and the latter for a 3d polarization function.

The Rh–Rh bond length for DRTC was calculated to be 2.28 Å, a little shorter than the experimental value 2.39 Å. The force constant for Rh–Rh vibration was calculated to be 1.9 mdyne/Å, which corresponds to a frequency of 250 cm<sup>-1</sup>. This value may be compared with 350 cm<sup>-1</sup> in the Raman spectrum of solid Rh<sub>2</sub>(O<sub>2</sub>CMe)<sub>4</sub> [13]. The stabilization energy due to axial ligand addition was calculated to be 35.1 kcal/mol for L = OH<sub>2</sub>, 48.7 kcal/mol for L = NH<sub>3</sub>, and 48.4 kcal/mol for L = PH<sub>3</sub>. These values seem to be overestimates. For DRTC with L = PH<sub>3</sub>, the effect of phosphorus 3d orbitals was a change from 37.0 kcal/mol for calculation without d AOs to 46.6 kcal/mol for  $\zeta(3d) = 0.015$ , and 48.4 kcal/mol for  $\zeta(3d) = 0.43$ . Thus we report here the result obtained with  $\zeta(3d) = 0.43$  for L = PH<sub>3</sub>.

Fig. 2 shows a diagram for the MO energy levels of DRTC complexes. Only the MOs pertinent to the Rh–Rh bond are shown. The electronic configuration is calculated to be  $\pi^4\delta^2\pi^*4\delta^*2\sigma^2$  for L free, L = OH<sub>2</sub>, and NH<sub>3</sub>. For L = PH<sub>3</sub>, it is  $\delta^2\pi^4\pi^*4\delta^*2\sigma^2$ . The HOMO was calculated to be  $\sigma$  for all the complexes studied here. For DRTC with L = PH<sub>3</sub>, this is in accord with the ESR experiment [8]. In table 1, we have shown the MO coefficients of the HOMO and

Table 1  
MO coefficient of the HOMOs of dirhodium tetracarboxylate complexes obtained from the present calculation and from ESR

Site a)		Ligand free	Axial ligand AH <sub>n</sub>			From ESR data for Rh <sub>2</sub> (O <sub>2</sub> CR) <sub>4</sub> (PY <sub>3</sub> ) <sub>2</sub> <sup>† c)</sup>
			OH <sub>2</sub>	NH <sub>3</sub>	PH <sub>3</sub> b) (with d)	
Rh	4d <sub>z</sub> <sup>2</sup>	0.644	0.623	0.593	0.562	0.54 – 0.83
	5s	0.284	0.235	0.200	0.132	0.14 – 0.24
	5p <sub>z</sub>	–0.121	–0.210	–0.278	–0.334	–
A	ns	–	–0.074	–0.041	–0.085	0.19 – 0.27
	np <sub>z</sub>	–	0.007	0.100	0.096	0.30 – 0.37
	nd <sub>z</sub> <sup>2</sup>	–	–	–	0.069	–
H (ligand)	1s	–	0.051	0.025	0.054	–
max. coeff. in carboxylate		0.071	0.073	0.082	0.094	–

a) See fig. 1. b) The exponent of the 3d orbital of P is 0.43.

c) Absolute value obtained from ref. [8]. R = C<sub>2</sub>H<sub>5</sub>; PY<sub>3</sub> = P(Ph)<sub>3</sub>, P(OPh)<sub>3</sub>, P(OCH<sub>2</sub>)<sub>3</sub>CC<sub>2</sub>H<sub>5</sub>.

compared them with the values estimated by the ESR experiment for DRTC cations with phosphorus-centered ligands [8]. The present results for  $L = \text{PH}_3$  compare well with the ESR estimates, though  $3s$  and  $3p_z$  components of phosphorus are smaller. The present result shows an appreciable mixing of the outer  $5p_z$  AO of Rh into the HOMO. It is to be noted that for  $L$  free and  $L = \text{OH}_2$ , the present MO sequence is different from that of the SCF  $X\alpha$  SW calculations of Norman and Kolari [6]. They reported the configuration  $\sigma^2\pi^4\delta^2\pi^*4\delta^*2$  where the HOMO is a  $\delta^*$  orbital. The same was true for the corresponding cation radical [7].

In fig. 2, it is seen that all the MO levels are raised by the addition of axial ligands (in agreement with the ligand field theory). The effect on the  $\sigma^*$  orbital is prominent, and next is the effect on the  $\sigma$  orbital (HOMO). The net gross charge of Rh obtained by a Mulliken population analysis was +0.70 (ligand free), +0.61 ( $L = \text{OH}_2$ ), +0.57 ( $L = \text{NH}_3$ ), and +0.41 [ $L = \text{PH}_3$  with  $d(\zeta = 0.43)$ ], showing charge transfer from axial ligands to Rh. The interaction is large when  $L = \text{PH}_3$ . The charge on the carboxylate ligand was very insensitive to the additions and the nature of the axial ligands ( $-0.36$  to  $-0.37$  on O, +0.30 on C, and +0.05 to +0.07 on H for all complexes studied here).

The nature of the charge-transfer interaction between DRTC and the axial ligand is explained with the use of an orbital correlation diagram in fig. 3. The charge transfer occurs from the lone pair of the axial ligand to the vacant non-bonding  $n\sigma^*$  (mainly  $5p_z$  and  $4d_{z^2}$  of Rh) and  $n\sigma$  (mainly  $5s$  and  $5p_z$  of Rh) MOs of DRTC. This is the so-called HOMO–LUMO interaction. In  $\sigma^*$  symmetry, the HOMO is the antisymmetric combination of lone pairs of ligands (denoted as

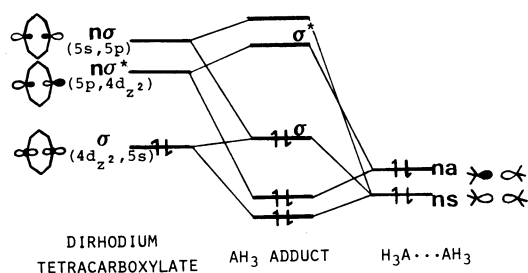


Fig. 3. Nature of the charge-transfer interaction in dirhodium tetracarboxylate complexes.

$na$ ) and the LUMO is the  $n\sigma^*$  orbital of DRTC. In  $\sigma$  symmetry, the HOMO is the symmetric combination of lone pairs ( $ns$ ) and the LUMO is the  $n\sigma$  MO of DRTC. The  $\sigma$  MO of DRTC (HOMO of DRTC) also interacts with  $ns$  and  $n\sigma$ . Since three levels are involved in  $\sigma$  symmetry, the  $\sigma$  MO of the adduct is not destabilized so much as the  $\sigma^*$ . Therefore, the  $\sigma$  MO of the adduct is *weakly* anti-bonding between Rh and P (or N or O). This is seen in table 1. The above HOMO–LUMO interactions should become stronger as the ionization potential of the axial ligand decreases. Then  $\text{PH}_3$  (IP = 9.9 eV) would be the strongest ligand, next is  $\text{NH}_3$  (IP = 10.9 eV), and  $\text{H}_2\text{O}$  (IP = 12.6 eV) the weakest<sup>†</sup>. Further, as expected from fig. 3, the outer  $5p_z$  AO of Rh mixes into the  $\sigma$  MO of the adduct through the addition of the ligand. As seen in table 1, the extent is largest for  $L = \text{PH}_3$  and smallest for  $L = \text{OH}_2$ , as expected. Conversely, the weights of  $4d_{z^2}$  and  $5s$  AOs decrease monotonically in the order  $L = \text{OH}_2, \text{NH}_3$  and  $\text{PH}_3$ . It will be interesting whether such a change will be observed by ESR.

Table 2 shows the change in valence AO population due to the axial ligand addition. In accord with the re-

<sup>†</sup> The ionization potentials in parentheses are experimental values [14]. The calculated values are 8.2, 9.5, and 10.7 eV for  $\text{PH}_3, \text{NH}_3$ , and  $\text{OH}_2$ , respectively.

Table 2  
Change in valence AO population by axial ligand addition

Site	AO a)	Axial ligand		
		$\text{OH}_2$	$\text{NH}_3$	$\text{PH}_3$
Rh	$4d_x^2, 4d_y^2, 4d_{xy}$	-0.019	-0.031	-0.017
	$4d_z^2$	-0.025	-0.045	-0.038
	$4d_{xz}, 4d_{yz}$	0.000	-0.002	-0.038
	$5s$	-0.066	-0.091	-0.138
	$5p_x, 5p_y$	0.010	-0.004	0.022
	$5p_z$	0.188	0.297	0.488
carboxylate		0.031	0.037	0.015
axial ligand	$ns$	-0.067	-0.006	-0.154
	$np_z$	0.015	-0.167	-0.152
	$np_x, np_y$	0.022	0.148	0.094
	$nd_x^2, \dots, nd_{xz}$	—	—	0.064
	$1s$ (H)	-0.063	-0.061	-0.056

a) See fig. 1.

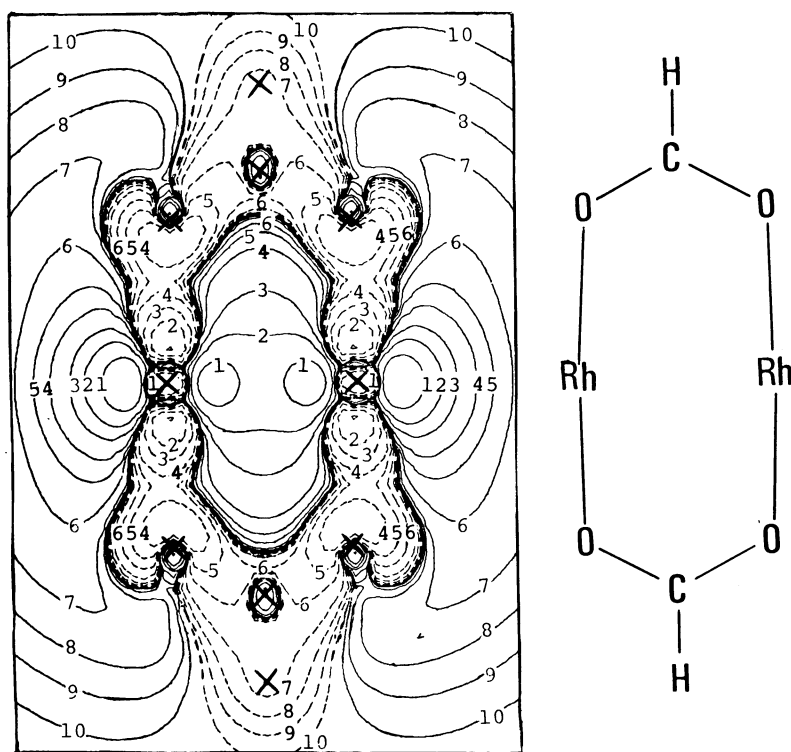


Fig. 4. Localized MO for the  $\sigma$  bond between Rh atoms in dirhodium tetracarboxylate. The skeleton on the right-hand side shows the plane of intersection. Solid and broken lines correspond, respectively, to the plus and minus signs in the MO. The numbers 1–10 on contours correspond to the contour values 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.002, 0.001, 0.0005, 0.0002, respectively.

sults of fig. 3 and table 1, the density increases mostly in the  $5p_z$  AO of Rh and decreases in the  $ns$  and  $np_z$  AOs of ligands (the lone-pair orbital is a hybrid of  $ns$  and  $np_z$  AOs). Again, the change is largest for  $L = \text{PH}_3$ . A small amount of back-donation is seen in the  $2p_x$  and  $2p_y$  AOs of  $\text{OH}_2$  and  $\text{NH}_3$ . For  $\text{PH}_3$ , it occurs in  $3p_x$ ,  $3p_y$ , and outer  $3d$  AOs. However, the participation of the  $3d$  orbitals is small.

In order to see the nature of the Rh–Rh bond, we have calculated localized molecular orbitals (LMOs) of DRTC. We have used the density localization method of Boys [15]. The energy localization method by Edmiston and Ruedenberg [16] is very time consuming for molecules of this size. The bonding  $\sigma$  LMO is displayed in fig. 4, while the LMO obtained by mixing orbitals of  $\pi$ ,  $\pi^*$ ,  $\delta$ , and  $\delta^*$  symmetries is displayed in fig. 5. They are the results of localization applied to 35 occupied orbitals from the HOMO (the total number of occupied orbitals is 91).

The  $\sigma$  LMO (fig. 4) shows a bonding nature between two Rh atoms and between Rh and oxygen of the carboxylate ligands. However, the bonding nature of Rh–Rh seems to be weak, since the electron density is not highest in the middle of the bond but in the atomic regions just inside the respective Rh atoms. The density is also high in the outside regions of the bond, showing a non-bonding character of this orbital. Thus, the  $\sigma$  LMO shows a weak bond between Rh atoms with non-bonding nature. The LMOs obtained by mixing MOs of  $\pi$ ,  $\pi^*$ ,  $\delta$ , and  $\delta^*$  symmetries are localized on one of the Rh atoms (fig. 5). This is natural, since mixing  $\pi$  and  $\pi^*$  ( $\delta$  and  $\delta^*$ ) MOs results in a localization on one of the component  $d_{yz}$  ( $d_{xy}$ ) AOs. The contour on the right-hand side of fig. 5 shows the  $d_{yz}$  AO of the *free* Rh atom. It is seen that the LMO in fig. 5 is very similar to the  $d_{yz}$  AO of the free atom. This fact suggests that the electrons in these LMOs are non-bonding and essentially as in the free atoms. This

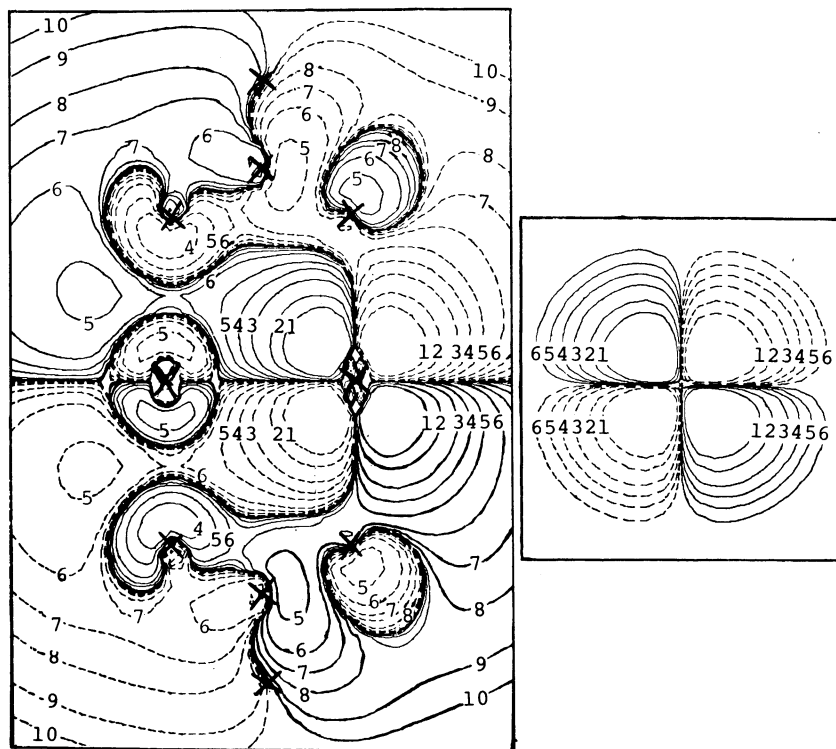


Fig. 5. Localized MO obtained from  $\pi$ ,  $\pi^*$ ,  $\delta$ , and  $\delta^*$  MOs in dirhodium tetracarboxylate. The plane of intersection is the same as in fig. 4. The contour on the right-hand side shows the  $d_{yz}$  AO on the *free* Rh atom. Solid and broken lines correspond, respectively, to the plus and minus signs in the MO. The numbers 1–10 on contours correspond to the contour values 0.1, 0.05, 0.02, 0.01, 0.005, 0.002, 0.001, 0.0005, 0.0002, 0.0001, respectively.

analysis shows that the Rh–Rh in DRTC forms a *weak* single bond.

### 3. Concluding remarks

We have studied the electronic structure of DRTC complexes by the *ab initio* SCF MO method. The nature of the Rh–Rh bond and the interaction between DRTC and axial ligands ( $\text{OH}_2$ ,  $\text{NH}_3$ , and  $\text{PH}_3$ ) have been clarified. For  $\text{L} = \text{PH}_3$ , the electronic configuration is calculated to be  $\delta^2\pi^4\pi^*\delta^*2\sigma^2$ ; i.e. the Rh–Rh bond is single and the HOMO has  $\sigma$  symmetry. This is in accord with a recent ESR experiment [8]. For  $\text{L} = \text{OH}_2$  and  $\text{L}$  free, the HOMO was also calculated to be  $\sigma$ . This differs from the results of SCF  $X\alpha$  SW calculations [6,7]. The reason for this difference needs to be studied.

In this communication we neglected electron correlation and relativistic effects. Benard and Veillard [17,18] have studied in detail the effect of electron correlation for quadruply bonded binuclear complexes like  $\text{Cr}_2(\text{O}_2\text{CH})_4$  and  $\text{Mo}_2(\text{O}_2\text{CH})_4$ . From the study of Hartree–Fock instability, it was concluded that the electron correlation should be important for *multiply* bonded binuclear complexes, while for *non-bonding* and *singly* bonded complexes, the Hartree–Fock description should be adequate [18]. This result may support the validity of the present result, since the single-bond nature of Rh–Rh in DRTC complexes is now well established. The fact that the Rh–Rh length in DRTC was calculated reasonably by the present method (calculated 2.28 Å; experimental 2.39 Å) is also support (see ref. [17]). Nevertheless, the role of electron correlation in the present system is now being studied.

After completion of this study, Professors F.A. Cotton and B.E. Bursten kindly informed us that their SCF  $X\alpha$  SW calculation for DRTC with  $L = PH_3$  has given a  $\sigma$  MO as HOMO, though it is largely of phosphine character.

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