

Non-Empirical Pseudopotentials (PSIBMOL Algorithm) for Molecular Calculations: The $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ Complex

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The electronic structure of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in the ground state is computed using the recently proposed PSIBMOL (Pseudo-potentials + IBMOL/H) formalism. The drawing of the total and differential isoelectronic contour maps supports the idea that there does not exist any rhodium-rhodium bond in such a binuclear complex, the origins of the preferred bent conformation having to be found elsewhere.

Key words: $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ – Non-empirical pseudopotentials

$\text{Rh}_2\text{Cl}_2(\text{CO})_4$ is the simplest member of those dirhodium complexes which are characterized by the now classical “bent” structure (Fig. 1) as well in the solid state [1] as in solution [2]. Such a structure constituted for many years a challenge for the theoretician: is the bending of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ due to the existence of a (Rh–Rh) binding interaction or to something else?

Using the analogy of the (Fe–Fe) bond in $\text{Fe}_2\text{X}_2(\text{CO})_6$ and of a (Co–Co) bond in $\text{Co}_2\text{X}_2(\text{CO})_6$ [3], Dahl *et al.* [1] proposed a “bent” (Rh··Rh) bond in $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. On the other hand, Norman and Gmur [4] concluded from $X\alpha$ calculations that there could not be any rhodium-rhodium binding interaction in the binuclear complex.

Having successfully tested the PSIBMOL (Pseudo-potentials + IBMOL/H) algorithm [5] on several transition metal derivatives [6], we have applied this technique to the study of the electronic structure in the ground state of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. The geometry we used is the experimental one proposed by Dahl [1] for the bent C_{2v} conformation (Fig. 1). The bond lengths and the valency angles were kept constant for the planar conformation, allowing the dihedral angle to vary.

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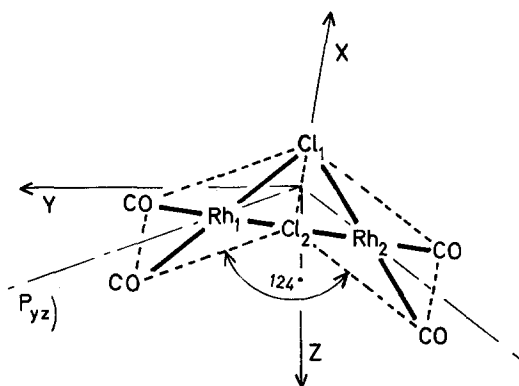


Fig. 1. Bent preferred conformation of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ and reference axes

The Rh, Cl, C and O atomic basis sets were optimized using the pseudopotential atomic program [7] and the pseudo-potentials of Tables 1 and 2. The four primitive Gaussians of each type are contracted in two contracted Gaussians in order to perform a calculation of "double-zeta" quality for the valence basis set. The size of the total basis set is 144 contracted Gaussians and this is practically the limit of what we can do with an IBM 370/168 (CIRCE, CNRS, Orsay, France) computer. The starting eigenvectors were provided by a preliminary extended CNDO [8] calculation and thus, the convergence of the SCF iterative process appears to be quite satisfactory and rapid.

Table 3 gathers the SALC (Symmetry adapted linear combinations) for the bent (C_{2v}) and the planar (D_{2h}) conformations. These linear combinations are written

Table 1. Parameters n_{il} , α_{il} and C_{il} of the radial components $W_i(r)$ of the pseudo-potentials for C, O and Cl (a.u.)

$$W_i(r) = \sum_l C_{il} r^{n_{il}} e^{-\alpha_{il} r^2}$$

Atom	Configuration	Atomic state		z	l	n_{il}	α_{il}	C_{il}	
C	$2s^2 2p^2$	3P	4	0	-2	0.65084	1.15210		
						2	0.65084	-0.22676	
	$2s^2 2p^2$	3P	4	1	0	7.22228	-2.27843		
O	$2s^2 2p^4$	3P	6	0	-2	1.22041	1.20971		
						2	1.22041	-0.84924	
	$2s^2 2p^4$	3P	6	1	0	13.73824	-3.25230		
Cl	$3s^2 3p^5$	2P	7	0	-2	0.80270	3.09806		
						2	0.80270	-0.54632	
						-2	0.75390	2.13242	
							2	0.75390	-0.33528
	$3s^2 3p^4 3d^1$	4D	7	2	0	7.23767	-14.57895		

Table 2. Parameters n_{ii} , α_{ii} and C_{ii} of the radial components $W_i(r)$ of the pseudo-potentials for Rh (a.u.):

$$W_i(r) = \sum_i C_{ii} r^{n_{ii}} e^{-\alpha_{ii} r^2}$$

Atom	Configuration	Atomic state	z	l	n_{ii}	α_{ii}	C_{ii}
Rh	5s ¹ 4d ⁸	⁴ F	9	0	-2	0.47577	10.11498
					2	0.47577	-0.16994
	5p ¹ 4d ⁸	⁴ D	9	1	-2	0.47391	12.08559
					2	0.47391	-0.03591
	5s ¹ 4d ⁸	⁴ F	9	2	-2	1.61652	0.93665
					2	1.61652	-7.49221

Table 3. Symmetry adapted linear combinations for Rh₂Cl₂(CO)₄^a

C_{2v}	D_{2h}	Rhodium AOs combinations	Chlorines AOs combinations
A_1	$\left\{ \begin{array}{l} A_g \\ B_{1u} \end{array} \right.$	$S_1 + S_2, Y_1 - Y_2, dZ_1^2 + dZ_2^2,$ $dX^2 - Y_1^2 + dX^2 - Y_2^2$	$S_1 + S_2, X_1 - X_2, dZ_1^2 + dZ_2^2,$ $dX^2 - Y_1^2 + dX^2 - dY_2^2$
		$Z_1 + Z_2, dYZ_1 - dYZ_2$	$Z_1 + Z_2, dXZ_1 - dXZ_2$
A_2	$\left\{ \begin{array}{l} B_{1g} \\ A_u \end{array} \right.$	$X_1 - X_2, dXY_1 + dXY_2$	$Y_1 - Y_2, dXY_1 + dXY_2$
		$dXZ_1 - dXZ_2$	$dYZ_1 - dYZ_2$
B_1	$\left\{ \begin{array}{l} B_{2g} \\ B_{3u} \end{array} \right.$	$dXZ_1 + dXZ_2$	$Z_1 - Z_2, dXZ_1 + dXZ_2$
		$X_1 + X_2, dXY_1 - dXY_2$	$S_1 - S_2, X_1 + X_2, dZ_1^2 - dZ_2^2,$ $dX^2 - Y_1^2 - dX^2 - Y_2^2$
B_2	$\left\{ \begin{array}{l} B_{3g} \\ B_{2u} \end{array} \right.$	$Z_1 - Z_2, dYZ_1 + dYZ_2$	$dYZ_1 + dYZ_2$
		$S_1 - S_2, Y_1 + Y_2, dZ_1^2 - dZ_2^2,$ $dX^2 - Y_1^2 - dX^2 - Y_2^2$	$Y_1 + Y_2, dXY_1 - dXY_2$

^aThe two rhodium atoms are located in the $y \circ z$ plane; the two chlorine atoms are on the x axis. In the D_{2h} conformation, these four atoms are in the $x \circ y$ plane, the two rhodiums being now on the y axis.

in such a way as to make the ($C_{2v} \rightarrow D_{2h}$) energy levels splitting conspicuous. The eigenvalues of the highest occupied MO are found in Table 4. These 14 MO correspond to the Rh(Cl)₂Rh part of the complex, the 22 lowest ones being related to the (Rh-C) and (C-O) bonds.

The 14 MO of Table 4 are built from the 4d AO of rhodium and the 3p AO of chlorine and are bonding and antibonding combinations of the 4d AO of the rhodium atoms. Each rhodium atom being involved in a distorted D_{4h} ligand field, the theory predicts that, using the reference axes of the Fig. 1, the $4d_{xz}$, $4d_{yz}$, $4d_{x^2-y^2}$ and $4d_{z^2}$ will only play a role in the MO's corresponding to the Rh(Cl)₂Rh pattern.

A detailed analysis of the main components of the MO (Table 4) and of the electronic populations (Table 5) proves that the $4d_{xy}$ AO of the rhodium atoms have

Table 4. Eigenvalues and main components of the 14 highest occupied MO for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$

MO	Bent conformation (C_{2v})		Planar conformation (D_{2h})		MO
	Components	Energy	Energy	Components	
$9b_2$	dYZ, dZ^2	-0.423	-0.405	dZ^2	$8a_g$
$9b_1$	dXZ	-0.429	-0.405	dZ^2	$7b_{2u}$
$11a_1$	dZ^2, dYZ	-0.433	-0.407	dXZ	$3b_{2g}$
$10a_1$	dYZ, dZ^2	-0.439	-0.419	dYZ	$3b_{1u}$
$8b_1$	dXY, pX	-0.463	-0.444	dXY, pX	$6b_{3u}$
$8b_2$	$dZ^2, dX^2 - Y^2, pY$	-0.466	-0.463	$dX^2 - Y^2, pY$	$6b_{2u}$
$7a_2$	dXZ, dXY	-0.486	-0.470	$dX^2 - Y^2, pX$	$7a_g$
$9a_1$	$dX^2 - Y^2, dYZ, pX$	-0.492	-0.471	dYZ	$2b_{3g}$
$7b_2$	dYZ, dZ^2	-0.506	-0.475	dXZ	$2a_u$
$6a_2$	dXY, pY	-0.526	-0.510	dXZ, pZ	$2b_{2g}$
$7b_1$	dXZ, pZ	-0.536	-0.511	dXY, pY	$5b_{1g}$
$8a_1$	dYZ, dZ^2, pZ	-0.544	-0.521	dYZ, pZ	$2b_{1u}$
$6b_2$	$dX^2 - Y^2, dYZ, pY$	-0.550	-0.534	$dX^2 - Y^2, pY$	$5b_{2u}$
$7a_1$	$dX^2 - Y^2, dYZ, pX$	-0.596	-0.574	$dX^2 - Y^2, pX$	$6a_g$
E_T		-159.163838	-159.157284		

a negligible contribution to the MO's in question. The molecule being constituted by two square-planar entities bridged by chlorines, a rhodium-rhodium "bond" would correspond to a linear combination of $4d_{yz}$ and $4d_{z^2}$ AO of the two metallic atoms.

Looking at Table 4, it appears that the (C_{2v}) $11a_1$ and the (D_{2h}) $8a_g$ MO's have a positive (Rh–Rh) overlap population. But it is also seen that the corresponding anti-bonding (C_{2v}) $9b_2$ and (D_{2h}) $7b_{2u}$ MO's have a negative (Rh–Rh) overlap population. Practically this cancels the previous positive one. In other words, the binding effects of the antisymmetrical combination of the $4d_{yz}$ AO's and of the symmetrical combination of $4d_{z^2}$ AO's (for the C_{2v} conformation) are counter-balanced by the MO which are built using the reverse combinations of the same orbitals.

Such a "zero balance" is supported by the global (Rh–Rh) overlap populations being negative, as well for the bent (-0.324) as for the planar (-0.342) conformation. Moreover, in order to visualize more definitely the antagonist effects of the two MO's we discussed above, we computed the total and differential molecular electron densities – as defined by Daudel *et al.* [9] – for the C_{2v} and D_{2h} forms either in the $y \circ z$ plane (Figs. 2 and 3) or in the $x \circ z$ plane (Figs. 4 and 5). The $11a_1$ and $9b_2$ density maps are given in Figs. 6 and 7. Figs. 3 and 5 demonstrate clearly that there does not exist any rhodium-rhodium bond in $\text{Rh}_2\text{Cl}_2(\text{CO})_4$, because no electron density is found between the two rhodiums. Moreover, Figs. 6 and 7 visualize the antagonistic effects discussed above.

However, Table 4 shows that the C_{2v} form is preferred over the D_{2h} one by 6.55×10^{-3} a.u., i.e. about 4.1 kcal/mole. It may be noticed that an EHT cal-

Table 5. Mulliken population analysis for the bent (*C*_{2v}) and planar (*D*_{2h}) conformations of Rh₂Cl₂(CO)₄

Orbital	<i>C</i> _{2v}	<i>D</i> _{2h}	Free CO
Rh 4s	0.4920	0.4210	
4p _x	0.3290	0.3264	
4p _y	0.3116	0.3866	
4p _z	0.1243	0.0356	
3d _{xx-yy}	1.8517	1.8419	
3d _{xy}	0.5631	0.4721	
3d _{xz}	1.6481	1.8642	
3d _{yz}	1.9025	1.8289	
3d _{z²}	1.8786	1.9342	
Charge	-0.1109	-0.0178	
Cl 3s	1.7194	1.7009	
3p _x	1.8240	1.8238	
3p _y	1.7133	1.6945	
3p _z	1.8366	1.9002	
3d	0.0380	0.0354	
Charge	-0.1313	-0.1548	
C 2s	1.5594	1.5721	1.8023
2p _x	0.7455	0.7497	0.7242
2p _y	0.6929	0.7233	0.6606
2p _z	0.6173	0.5922	0.5207
Charge	+0.3849	+0.3627	+0.2922
O 2s	1.8041	1.8035	1.8049
2p _x	1.4574	1.4611	1.4753
2p _y	1.4762	1.4593	1.4896
2p _z	1.5261	1.5525	1.5224
Charge	-0.2638	-0.2764	-0.2922
Overlap			
Rh-Rh	-0.324	-0.342	
Cl-Cl	-0.402	-0.322	
Rh-Cl	+0.295	+0.303	
Rh-C	+0.838	+0.893	
C-O	+1.352	+1.334	+1.153

culation by Hoffmann [10] had led to the reverse. Our result would be completely unambiguous provided the correlation energies for the two forms, computed with the help in a further step of Malrieu CIPSI's configuration interaction process [11], would be identical. However, it seems that a configuration interaction generally doesn't change an *ab initio* "double-zeta" calculation. Unfortunately our computer facilities do not allow us to test this.

The preference of the binuclear rhodium complex for a *bent* conformation may be explained by a detailed analysis of the MO eigenvalues and of the electronic populations. Indeed, the (Rh-Rh) overlap population is less antibonding for the

C_{2v} form than for the D_{2h} one. Moreover, in the bent conformation, the energies of the $11a_1$ and $9b_2$ MO's (-0.433 and -0.423 a.u.) are lower – and slightly different from each other – than the corresponding $8a_g$ and $7b_{2u}$ orbitals (-0.405 and -0.405 a.u.) for the planar form. The two bonding ($8a_g$) and antibonding ($7b_{2u}$) effects cancel each other almost exactly in the D_{2h} conformation whereas the bonding ($11a_1$) effect is slightly predominant over the antibonding ($9b_2$) one in

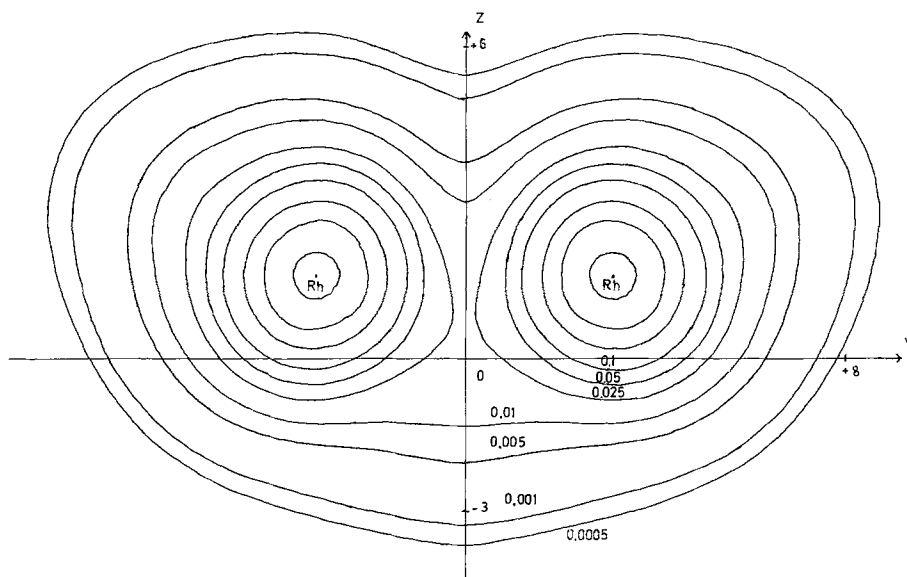


Fig. 2. Total isoelectronic density map (in $e \cdot \text{a.u.}^{-3}$) for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in the y - z plane (bent conformation)

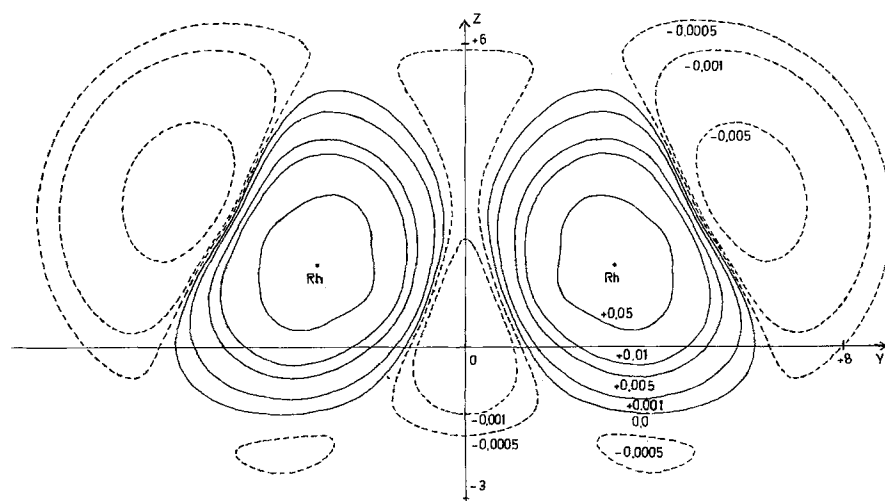


Fig. 3. Differential isoelectronic density map (in $e \cdot \text{a.u.}^{-3}$) for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in the y - z plane (bent conformation)

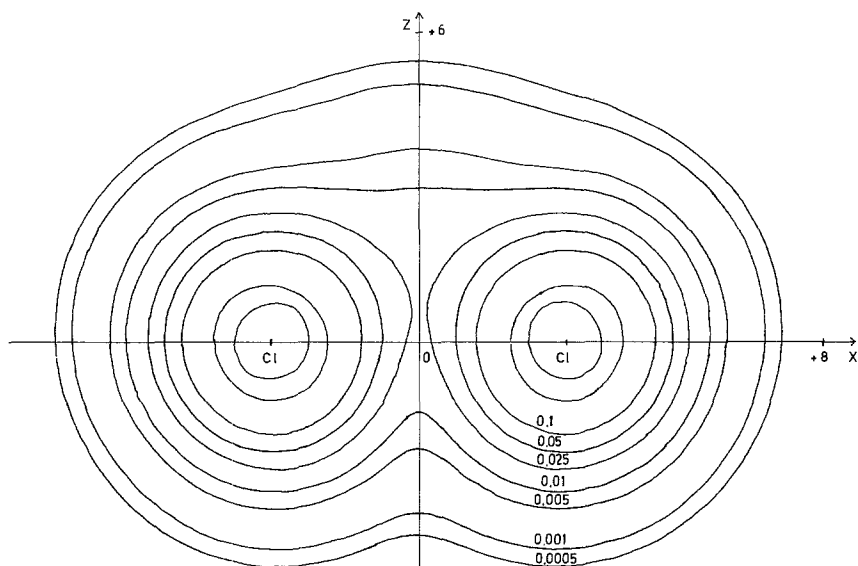


Fig. 4. Total isoelectronic density map (in $e \cdot \text{a.u.}^{-3}$) for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in the xoz plane (bent conformation)

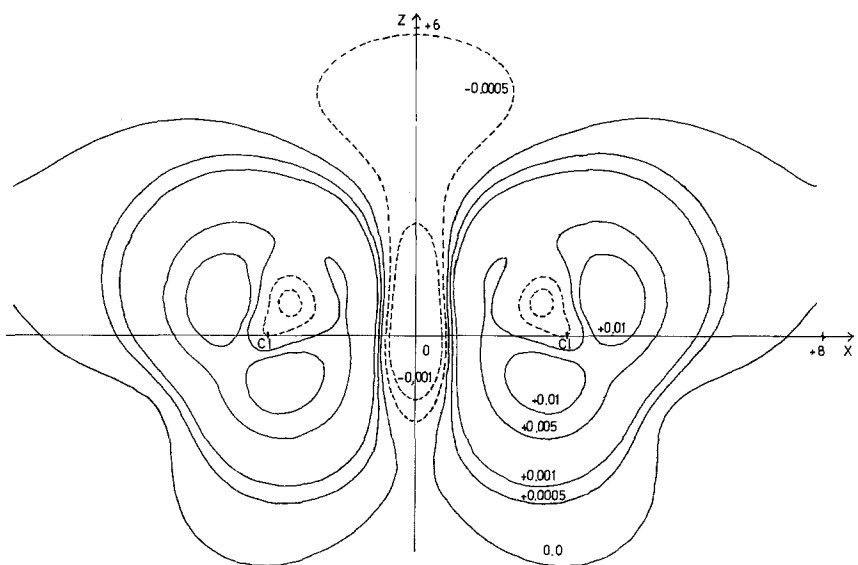


Fig. 5. Differential isoelectronic density map (in $e \cdot \text{a.u.}^{-3}$) for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in the xoz plane (bent conformation)

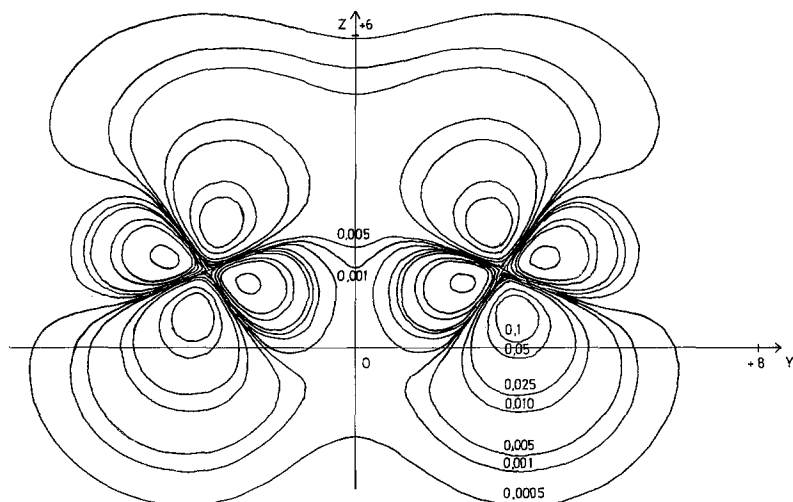


Fig. 6. Contours map (in e·a.u.⁻³) for the $11a_1$ MO of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ (bent conformation)

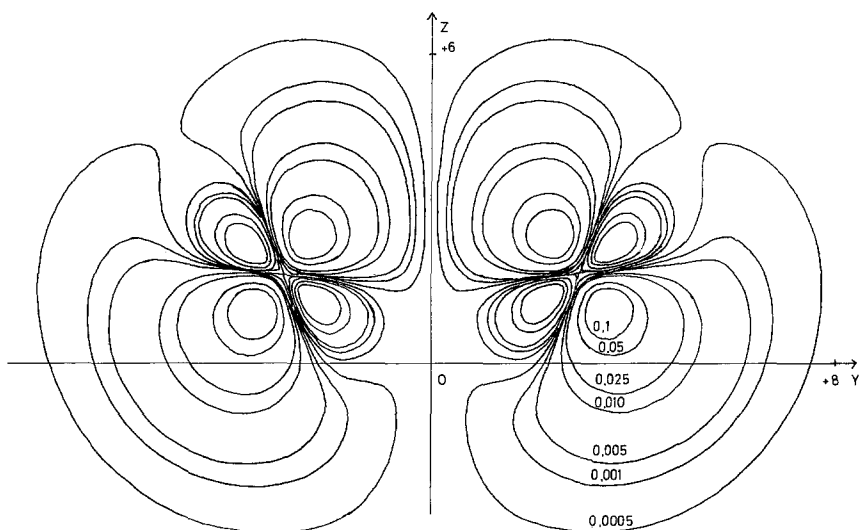


Fig. 7. Contours map (in e·a.u.⁻³) for the $9b_2$ MO of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ (bent conformation)

the preferred C_{2v} conformation. We notice finally that Norman and Gmur's $X\alpha$ calculations [4] lead to the same conclusion.

Our conclusions are therefore that the PSIBMOL calculation of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ supports the suggestion of the *non*-existence of a rhodium-rhodium bond, but that the origins of the preferred bent conformation are still somewhat uncertain. However, only by performing a full configuration interaction will it be possible to reach a complete understanding of this very intricate molecule.

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