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Comparative Study of Molecular Orbitals of Ruthenium (II) Chloride and Ruthenium (II) Iodide Based on Molecular Mechanics

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ABSTRACT

We have studied the molecular orbitals of ruthenium halides, in order to study the extent of contribution of 4d, 5s and 5p orbitals in the formation of molecular orbitals. The 3D modeling and geometry optimization of the ruthenium halides have been done by CAChe software using molecular mechanics with EHT option. Eigenvector analysis shows that 4dx^2-y^2 and 4dxy orbitals of ruthenium play a major role in bonding between ruthenium and halogens, 5s orbital is next and 5p orbitals have a negligible role. There is a difference in energy levels of s and p orbitals of chloride and iodide are 0.1691 and 0.7472 respectively. The overlap population analysis shows that the nonbonding orbitals are present in 6th and 7th molecular orbitals in both. No molecular orbital is formed by only two atomic orbitals. All molecular orbitals have contribution from many atomic orbitals; the difference is only in extent of involvement.

Keywords: Ruthenium (II) chloride, ruthenium (II) iodide, sd hybridization, population analysis, overlap population analysis, eigenvector, eigenvalues.

INTRODUCTION

In the recent years Landis presented the result of DFT calculation of transition metal hydride [1-3]. He also gave the results of an NBO analysis of the transition metal-hydrogen bonds, which show dominantly sdn hybridized bond orbitals and negligible np participation [1]. However, there is a serious technical flaw in the analysis. The NBO method requires preselection of those orbitals, which are considered as valence orbitals, and may become occupied in the population analysis. In the last few decades, there has been a phenomenal advancement in theoretical inorganic chemistry. Commercial programs incorporating the latest methods have become widely available, and are capable of providing more information about molecular orbitals with a simple input of chemical formula. The focus of attention has been on computational transition-metal chemistry [4, 5]. This is largely due to the successful employment of gradient corrected density functional theory in calculating molecule; particularly of the heavier atoms [6-9] and in the use of small-core relativistic effective core potential [10-12] which set the stage for calculation of geometries, bond energies, and chemical reaction and other important properties of transition metal compounds with impressive accuracy [9, 13, 14]. Application of molecular mechanics to organometallic and transition metal compounds is growing [15]. Molecular orbital parameters such as eigenvalues, eigenvectors and overlap matrix are well calculated with this method. In this paper we present the comparative study of ruthenium (II) chloride and ruthenium (II) iodide based on eigenvalues, eigenvector, overlap matrix, population analysis and overlap population analysis, in order to study the extent of contribution of 4d, 5s and 5p orbitals in the formation of molecular orbitals. Such a quantitative study will provide correct information about the involvement of 5p orbital of ruthenium in bonding.

MATERIALS AND METHODS

The study materials of this paper are ruthenium (II) chloride and ruthenium (II) iodide. The 3D modeling and geometry optimization of the halide have been done by CAChe software using molecular mechanics with EHT option. Eigenvalues, eigenvectors and overlap matrix values have been obtained with the same software, using the same option. With the help of these values, eigenvector analysis, magnitude of contribution of atomic orbital in MO formation and population analysis have been made and discussed. The method adopted for various calculations is based on the following principles.

The molecular orbitals are formed by the linear combination of basis functions. Most molecular quantum-mechanical methods (such as- SCF, CI etc.) begin the calculation with the choice of a basis functions χ_r, which are used to express the MOs ϕ_i as $\phi_i = \Sigma_i c_{ri} \chi_r$ (c = coefficient of χ, r = number of atomic orbital, i = molecular orbital number). The use of an adequate basis set is an essential requirement for the calculation. The basis functions are usually taken as AOs. Each AO can be represented as a linear combination of one or more Slater-type orbitals (STOs) [15, 25, 26]. Each molecular orbital ϕ_i is expressed as $\phi_i = \Sigma_i c_{ri} \chi_r$, where, the χ_r 's are the STO basis functions. Here we use the STO–6G basis set (which is contracted Gaussian) [27-30] for the SCF calculation.

The coefficients in linear combination for each molecular orbital being found by solution of the Roothaan equation [31]. The most efficient way to solve the Roothaan equation is to use matrix–algebra methods. In matrix–algebra methods, the matrix elements are computed [32], and the secular equation is solved to give the set of orbital energies (i.e. eigenvalues). These orbital energies [33-35] are used to solve Roothaan equations for the set of coefficients (i.e. eigenvectors) giving a set of molecular orbitals. The calculations are done using a computer.
By the above calculation, the values of orbital energies (eigenvalues) and eigenvectors (coefficients) have been calculated.

A widely used method to analyze SCF wave function is population analysis, introduced by Mulliken [36, 37]. He proposed a method that apportions the electrons of an n–electron molecule into net populations n_r in the basis functions χ_r and overlap populations n_{r-s} for all possible pairs of basis functions.

For the set of basis functions $\chi_1, \chi_{2,\ldots,}\, \chi_b$, each molecular orbital ϕ_i has the form $\phi_i = \sum_s c_{si}\chi_s = c_{1i}\chi_1 + c_{2i}\chi_2 + \ldots + c_{bi}\chi_b$. For simplicity, we shall assume that the c_{si}'s and χ_s's are real. The probability density associated with one electron in ϕ_i is (s and b are the number of the atomic orbital other than r)

$$|\phi_i|^2 = c_{1i}^2\chi_1^2 + c_{2i}^2\chi_2^2 + \ldots\ldots + 2c_{1i}c_{2i}\chi_1\chi_2 + 2c_{1i}c_{3i}\chi_1\chi_3 + 2c_{2i}c_{3i}\chi_2\chi_3 + \ldots\ldots$$

Integrating this equation over three-dimensional space and using the fact that ϕ_i and the χ_s's are normalized, we get

$$1 = c_{1i}^2 + c_{2i}^2 + \ldots\ldots\ldots + 2c_{1i}c_{2i}S_{12} + 2c_{1i}c_{3i}S_{13} + 2c_{2i}c_{3i}S_{23} + \ldots \qquad (3)$$

Where the S's are overlap integrals: $S_{12} = \int\chi_1\chi_2 dv_1 dv_2$, etc. Mulliken proposed that the terms in (3) be apportioned as follows. One electron in the molecular orbital ϕi contributes c_{1i}^2 to the net population in χ_1, c_{2i}^2 to the net population in χ_2, etc., and contributes $2c_{1i}c_{2i}S_{12}$ to the overlap population between χ_1 and χ_2, $2c_{1i}c_{3i}S_{13}$ to the overlap population between χ_1 and χ_3, etc.

Let there be n_i electrons in the molecular orbital ϕ_i (n_i = 0,1,2) and let $n_{r,i}$ and $n_{r\text{-}s,i}$ symbolize the contributions of electrons in the molecular orbital ϕ_i to the net population in χ_r and to the overlap population between χ_r and χ_s, respectively. We have

$$n_{r,i} = n_i\, c^2_{ri},$$
$$n_{r\text{-}s,i} = n_i\,(2c_{ri}\, c_{si}\, S_{rs})$$

Based on the above principle, the contribution of electrons in each occupied molecular orbital has been calculated with the help of eigenvector values and also calculated overlap population analysis for distinguishing the bonding, nonbonding and antibonding nature of molecular orbital.

RESULTS AND DISCUSSION

Ruthenium (II) chloride and ruthenium (II) iodide is triatomic molecule, having the following (Fig. 1.1, 1.2) optimized geometry [16, 17] as obtained from molecular mechanics [18-21] method.

The MOs of these halides (chloride and iodide) are formed by linear combination of 9 ruthenium orbitals and 4 orbitals from each halogen as detailed below-

Ru-1 = 5s, 5px, 5py, 5pz, $4dx^2\text{–}y^2$, $4dz^2$, 4dxy, 4dxz, 3dyz	= 9
X-2 = ns, npx, npy, npz	= 4
X-3 = ns, npx, npy, npz	= 4
	Total = 17

where X = Cl or I; n = 3 for Cl and n = 5 for I.

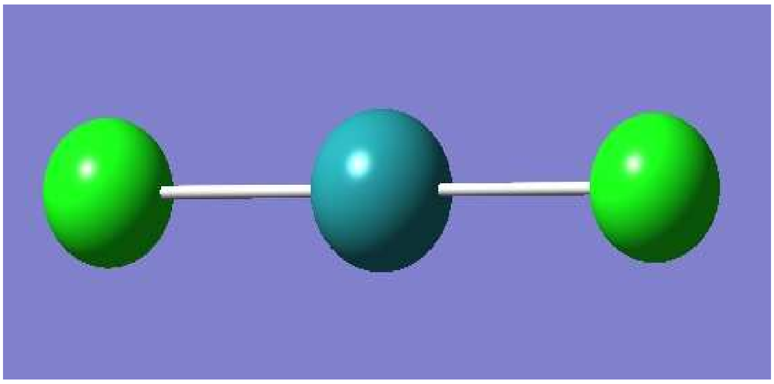

Fig.1.1: Optimized geometry of Ruthenium (II) Chloride.

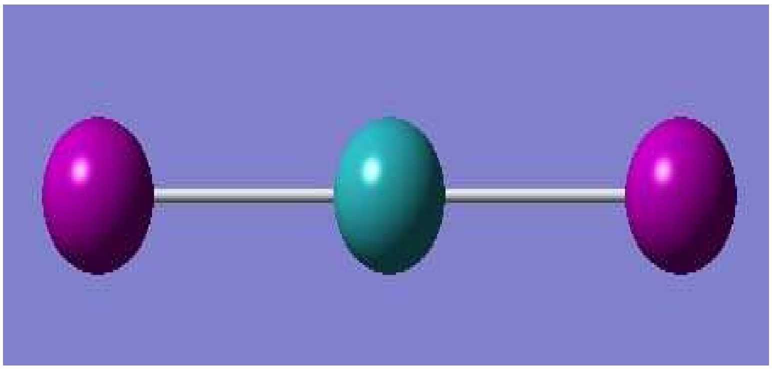

Fig.1.2: Optimized geometry of Ruthenium (II) Iodide.

In order to examine the contribution of various atomic orbitals in the formation of molecular orbitals the LCAO has been studied. The 17 AOs give LCAO approximations to the 17 MOs of ruthenium (II) halides. The various AOs are represented by χ and MOs by ϕ. χ_1 to χ_9 are 5s, 5px, 5py, 5pz, 4dx^2-y^2, 4dz^2, 4dxy, 4dxz, 4dyz, respectively and χ_{10} to χ_{13} and χ_{14} to χ_{17} are ns, npx, npy, npz for X-2 and X-3, respectively are atomic orbitals of halides.

The eigenvalues of 17 MOs (ϕ_1 to ϕ_{17}) of ruthenium (II) chloride are -0.9810, -0.9696, -0.5934, -0.5824, -0.5824, -0.5476, -0.5476, -0.5326, -0.5271, -0.5271, -0.4986, -0.4726, -0.4726, -0.2118, -0.2118, 0.1413 and 0.6063, respectively and of ruthenium (II) iodide are -0.6884, -0.6679, -0.5565, -0.5565, -0.5560, -0.5476, -0.5476, -0.4843, -0.4811, -0.4700, -0.4700, -0.4521, -0.4521, -0.2336, -0.2336, -0.0681 and 0.2251, respectively. The coefficients of χ are the eigenvector and overlap matrix which has been taken from Table-1.1, Table- 1.2 and Table- 2.1, Table- 2.2 respectively.

Table 1.1: Eigenvector values of molecular orbitals of Ruthenium (II) chloride.

Atom	AOs	Eigenvector values or coefficients of Atomic Orbitals																
	(χ)	**MO-1**	**MO-2**	**MO-3**	**MO-4**	**MO-5**	**MO-6**	**MO-7**	**MO-8**	**MO-9**	**MO-10**	**MO-11**	**MO-12**	**MO-13**	**MO-14**	**MO-15**	**MO-16**	**MO-17**
Ru-1	5s	-0.1029	0.0000	0.0966	-0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0000	0.0000	-0.4603	-0.0000	-0.0000	-0.0000	-0.0000	-1.1218	0.0000
	5px	-0.0000	-0.0688	-0.0000	0.0000	-0.0000	0.0000	0.0000	-0.1681	-0.0014	0.0000	0.0000	-0.0000	-0.0000	0.0111	0.0000	0.0000	1.4554
	5py	0.0000	-0.0007	0.0000	0.0000	-0.0000	-0.0000	-0.0000	-0.0018	0.1271	-0.0006	-0.0000	0.0000	0.0000	-1.0225	-0.0003	0.0000	0.0158
	5pz	-0.0000	-0.0000	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	0.0006	0.1271	-0.0000	-0.0000	0.0000	0.0003	-1.0226	-0.0000	-0.0000
	$4dx^2$-y^2	-0.1049	-0.0000	0.4628	-0.0027	0.0161	-0.0000	-0.4999	0.0000	0.0000	-0.0000	0.6669	0.0003	0.0146	-0.0000	-0.0000	-0.4071	0.0000
	$4dz^2$	0.0606	-0.0000	-0.2673	0.0000	-0.0000	-0.0000	-0.8660	-0.0000	-0.0000	0.0000	-0.3851	-0.0000	-0.0000	0.0000	0.0000	0.2351	-0.0000
	4dxy	-0.0023	0.0000	0.0100	0.1234	-0.7415	-0.0000	-0.0108	-0.0000	-0.0000	0.0000	0.0145	-0.0131	-0.6721	-0.0000	-0.0000	-0.0088	-0.0000
	4dxz	0.0000	-0.0000	-0.0000	0.7416	0.1234	0.0108	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.6722	-0.0131	0.0000	-0.0000	-0.0000	0.0000
	4dyz	0.0000	0.0000	0.0000	0.0080	0.0013	-0.9999	0.0000	-0.0000	0.0000	0.0000	-0.0000	0.0073	-0.0001	-0.0000	0.0000	-0.0000	-0.0000
Cl-2	3s	-0.6626	-0.6829	-0.1572	0.0000	-0.0000	-0.0000	-0.0000	0.0675	0.0000	-0.0000	-0.0028	-0.0000	-0.0000	0.0000	0.0000	0.3728	-0.5297
	3px	-0.0142	-0.0187	-0.4916	-0.0007	0.0043	-0.0000	0.0000	0.6403	-0.0074	0.0000	0.2812	-0.0001	-0.0064	-0.0028	-0.0000	-0.6084	0.6516
	3py	-0.0002	-0.0002	-0.0053	0.0660	-0.3966	-0.0000	-0.0000	0.0069	0.6796	-0.0032	0.0030	0.0115	0.5894	0.2616	0.0001	-0.0066	0.0071
	3pz	0.0000	-0.0000	-0.0000	0.3967	0.0660	0.0000	-0.0000	0.0000	0.0032	0.6796	0.0000	-0.5894	0.0115	-0.0001	0.2616	0.0000	-0.0000
Cl-3	3s	-0.6626	0.6829	-0.1572	-0.0000	0.0000	0.0000	-0.0000	-0.0675	0.0000	-0.0000	-0.0028	0.0000	0.0000	0.0000	0.0000	0.3728	0.5297
	3px	0.0142	-0.0187	0.4916	0.0007	-0.0043	-0.0000	0.0000	0.6403	-0.0074	0.0000	-0.2812	0.0001	0.0064	-0.0028	-0.0000	0.6084	0.6516
	3py	0.0002	-0.0002	0.0053	-0.0660	0.3966	-0.0000	-0.0000	0.0069	0.6796	-0.0032	-0.0030	-0.0115	-0.5894	0.2616	0.0001	0.0066	0.0071
	3pz	0.0000	0.0000	-0.0000	-0.3967	-0.0660	0.0000	-0.0000	0.0000	0.0032	0.6796	0.0000	0.5894	-0.0115	-0.0001	0.2616	0.0000	0.0000

Table 1.2: Eigenvector values of molecular orbitals of Ruthenium (II) iodide.

Atom	AOs	Eigenvector values or coefficients of Atomic Orbitals																
	(χ)	MO-1	MO-2	MO-3	MO-4	MO-5	MO-6	MO-7	MO-8	MO-9	MO-10	MO-11	MO-12	MO-13	MO-14	MO-15	MO-16	MO-17
Ru-1	5s	0.1682	0.0000	-0.0000	-0.0000	0.0083	-0.0000	-0.0000	0.0000	0.4973	-0.0000	0.0000	0.0000	-0.0000	0.0000	0.0000	-1.0160	0.0000
	5px	0.0000	-0.1190	0.0000	0.0000	0.0000	0.0000	-0.0000	0.2102	-0.0000	0.0000	-0.0013	0.0000	-0.0000	-0.0109	-0.0000	0.0000	1.3059
	5py	-0. 0000	-0.0013	0.0000	0.0000	-0.0000	-0.0000	0.0000	0.0023	-0.0000	-0.0005	0.1194	-0.0000	0.0000	1.0072	0.0023	0.0000	0.0142
	5pz	-0.0000	0.0000	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1194	0.0005	-0.0000	-0.0000	0.0023	-1.0073	-0.0000	0.0000
	$4dx^2$-y^2	0.2522	-0.0000	-0.0002	-0.0202	-0.6232	0.0000	0.4999	-0.0000	-0.4917	0.0000	-0.0000	-0.0001	0.0081	0.0000	0.0000	-0.3287	0.0000
	$4dz^2$	-0.1457	-0.0000	-0.0000	-0.0000	-0.3599	0.0000	0.8660	0.0000	0.2839	-0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.1898	-0.0000
	4dxy	0.0055	0.0000	0.0079	0.9309	-0.0135	0.0000	0.0108	0.0000	-0.0107	0.0000	-0.0000	0.0037	-0.3745	0.0000	0.0000	-0.0071	-0.0000
	4dxz	0.0000	0.0000	-0.9311	0.0079	-0.0000	0.0108	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	0.3745	0.0037	0.0000	-0.0000	0.0000	0.0000
	4dyz	0.0000	-0.0000	-0.0101	0.0001	0.0000	-0.9999	0.0000	0.0000	-0.0000	0.0000	0.0000	0.0041	0.0000	-0.0000	0.0000	0.0000	0.0000
I-2	5s	0.6043	-0.6703	0.0000	0.0000	0.2911	0.0000	0.0000	-0.1031	-0.0636	0.0000	-0.0000	-0.0000	0.0000	-0.0000	-0.0000	0.3208	-0.4207
	5px	-0.0470	-0.0091	-0.0000	-0.0023	0.3536	0.0000	0.0000	0.6191	-0.4060	0.0000	0.0075	-0.0001	-0.0064	-0.0022	0.0000	-0.5813	0.6031
	5py	-0.0005	-0.0001	0.0018	0.2067	0.0038	0.0000	0.0000	-0.0067	-0.0040	-0.0027	0.6879	-0.0068	0.6787	-0.2026	-0.0005	-0.0063	0.0065
	5pz	-0.0000	-0.0000	-0.2076	0.0018	0.0000	0.0000	0.0000	-0.0000	0.0000	0.6880	0.0027	-0.6787	-0.0068	-0.0005	0.2026	0.0000	-0.0000
I-3	5s	0.6043	0.6703	-0.0000	-0.0000	0.2911	0.0000	0.0000	0.1031	-0.0637	0.0000	-0.0000	0.0000	-0.0000	-0.0000	-0.0000	0.3208	0.4207
	5px	0.4070	-0.0091	0.0000	0.0023	-0.3536	-0.0000	-0.0000	-0.6191	0.4060	0.0000	-0.0075	-0.0001	0.0074	0.0022	0.0000	0.5813	0.6031
	5py	0.0005	-0.0001	-0.0018	-0.2076	-0.0038	0.0000	0.0000	-0.0067	0.0044	-0.0027	-0.6879	0.0068	-0.6787	-0.2026	-0.0005	0.0063	0.0065
	5pz	-0.0000	0.0000	0.2076	-0.0018	0.0000	0.0000	0.0000	0.0000	0.0000	0.6880	0.0027	0.6787	0.0068	-0.0005	0.2026	0.0000	0.0000

Table 2.1: Overlap matrix (Overlap integrals values) of Ruthenium (II) chloride.

AOs	**5s (Ru-1)**	**5px (Ru-1)**	**5py (Ru-1)**	**5pz (Ru-1)**	**$4dx^2$-y^2 (Ru-1)**	**$4dz^2$ (Ru-1)**	**4dxy (Ru-1)**	**4dxz (Ru-1)**	**4dyz (Ru-1)**	**3s (Cl-2)**	**3px (Cl-2)**	**3py (Cl-2)**	**3pz (Cl-2)**	**3s (Cl-3)**	**3px (Cl-3)**	**3py (Cl-3)**	**3pz (Cl-3)**
5s (Ru-1)	1.0000																
5px (Ru -1)	-0.0000	1.0000															
5py (Ru -1)	-0.0000	-0.0000	1.0000														
5pz (Ru -1)	0.0000	0.0000	0.0000	1.0000													
$4dx^2$-y^2 (Ru -1)	0.0000	0.0000	-0.0000	0.0000	1.0000												
$4dz^2$ (Ru -1)	-0.0000	-0.0000	-0.0000	0.0000	0.0000	1.0000											
4dxy (Ru -1)	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	1.0000										
4dxz (Ru 1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
4dyz (Ru -1)	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000	1.0000								
3s (Cl-2)	0.2270	0.3406	0.0037	0.0000	0.0994	-0.0574	0.0022	0.0000	0.0000	1.0000							
3px (Cl-2)	-0.3205	-0.3862	-0.0060	0.0000	-0.1310	0.0757	-0.0038	0.0000	0.0000	-0.0000	1.0000						
3py (Cl-2)	-0.0035	-0.0060	0.1707	0.0000	-0.0034	0.0008	0.0923	0.0000	0.0000	-0.0000	0.0000	1.0000					
3pz (Cl-2)	0.0000	0.0000	0.0000	0.1708	0.0000	0.0000	0.0000	0.0923	0.0010	0.0000	0.0000	0.0000	1.0000				
3s (Cl-3)	0.2270	-0.3406	-0.0037	0.0000	0.0994	-0.0574	0.0022	0.0000	0.0000	0.0004	-0.0027	-0.0000	0.0000	1.0000			
3px (Cl-3)	0.3205	-0.3862	-0.0060	0.0000	0.1310	-0.0757	0.0038	0.0000	0.0000	0.0027	-0.0108	-0.0001	0.0000	0.0000	1.0000		
3py (Cl-3)	0.0035	-0.0060	0.1707	0.0000	0.0034	-0.0008	-0.0923	0.0000	0.0000	0.0000	-0.0001	0.0011	0.0000	-0.0000	-0.0000	1.0000	
3pz (Cl-3)	0.0000	0.0000	0.0000	0.1708	0.0000	0.0000	0.0000	-0.0923	-0.0010	0.0000	0.0000	0.0000	0.0011	0.0000	0.0000	0.0000	1.0000

Table 2.2: Overlap matrix (Overlap integrals values) of Ruthenium (II) iodide.

AOs	5s (Ru-1)	5px (Ru-1)	5py (Ru-1)	5pz (Ru-1)	$4dx^2$-y^2 (Ru-1)	$4dz^2$ (Ru-1)	4dxy (Ru-1)	4dxz (Ru-1)	4dyz (Ru-1)	5s (I-2)	5px (I-2)	5py (I-2)	5pz (I-2)	5s (I-3)	5px (I-3)	5py (I-3)	5pz (I-3)
5s (Ru-1)	1.0000																
5px (Ru -1)	-0.0000	1.0000															
5py (Ru -1)	-0.0000	-0.0000	1.0000														
5pz (Ru -1)	0.0000	0.0000	0.0000	1.0000													
$4dx^2$-y^2 (Ru -1)	0.0000	0.0000	-0.0000	0.0000	1.0000												
$4dz^2$ (Ru -1)	-0.0000	-0.0000	-0.0000	0.0000	0.0000	1.0000											
4dxy (Ru -1)	-0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	1.0000										
4dxz (Ru 1)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000									
4dyz (Ru -1)	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0000	0.0000	-0.0000	1.0000								
5s (I-2)	0.1844	0.2783	0.0030	0.0000	0.0748	-0.0432	0.0016	0.0000	0.0000	1.0000							
5px (I-2)	-0.2793	-0.3722	-0.0053	0.0000	-0.1156	0.0667	-0.0032	-0.0000	-0.0000	-0.0000	1.0000						
5py (I-2)	-0.0030	-0.0053	0.1185	0.0000	-0.0026	0.0007	0.0605	-0.0000	0.0000	-0.0000	0.0000	1.0000					
5pz (I-2)	0.0000	0.0000	0.0000	0.1185	0.0000	0.0000	0.0000	0.0605	0.0007	0.0000	0.0000	0.0000	1.0000				
5s (I-3)	0.1844	-0.2783	-0.0030	0.0000	0.0748	-0.0432	0.0016	0.0000	0.0000	0.0001	-0.0006	-0.0000	0.0000	1.0000			
5px (I-3)	0.2793	-0.3722	-0.0053	0.0000	0.1156	-0.0667	0.0032	-0.0000	-0.0000	0.0006	-0.0024	-0.0000	0.0000	0.0000	1.0000		
5py (I-3)	0.0030	-0.0053	0.1185	0.0000	0.0026	-0.0007	-0.0605	-0.0000	0.0000	0.0000	-0.0000	0.0002	0.0000	-0.0000	-0.0000	1.0000	
5pz (I-3)	0.0000	0.0000	0.0000	0.1185	0.0000	0.0000	0.0000	-0.0605	-0.0007	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	1.0000

In order to examine the extent of involvement of 4d, 5s and 5p orbitals in the formation of molecular orbitals the values of coefficient of these orbitals have been added to see the total involvement in all the eleven MOs (ϕ_1-ϕ_{11}). The summation values of 4dxy, 4dxz, 4dx^2-y^2, 5s, 5px, 5py, and 5pz of ruthenium (II) chloride are 0.9025, 0.8758, 1.7533, 0.6598, 0.2383, 0.1302 and 0.1277, respectively and that of ruthenium (II) iodide are 0.9738, 0.9498, 1.8874, 0.6738, 0.3305, 0.1230 and 0.1199, respectively. The nonbonding orbitals 4dz^2 and 4dyz are excluded. It is clearly indicated that the maximum involvement is of 4dx^2-y^2 orbital and the minimum of 5pz orbital in both halides. In ruthenium (II) chloride the value of 5p orbitals are in the range 0.2383 to 0.1277 which is very low in comparison to d orbitals (dxy, dxz, dx^2-y^2) which is in the range 1.7533 to 0.8758 and the value for 5s is 0.6598; whereas in ruthenium (II) iodide the value of 5p orbitals are between 0.3305 to 0.1199 which is very low in comparison to d orbitals (dxy, dxz, dx^2-y^2) which is in the range 1.8874 to 0.9498. The value for 5s is 0.6738. So the involvement of 5p orbitals is negligible in both in comparison of 4d orbitals. The extent of involvement of 4d, 5s and 5p orbitals of ruthenium in the formation of MOs in the chloride and iodide is well demonstrated by the graph (Fig-2) drawn between the orbitals and the summation values of their coefficients. The graph showing below clearly shows that the involvement of p orbitals is negligible. The summation values are highest in case of iodide and lowest in chloride. It is perhaps on this account the splitting of d orbitals is maximum in iodide and minimum in chloride.

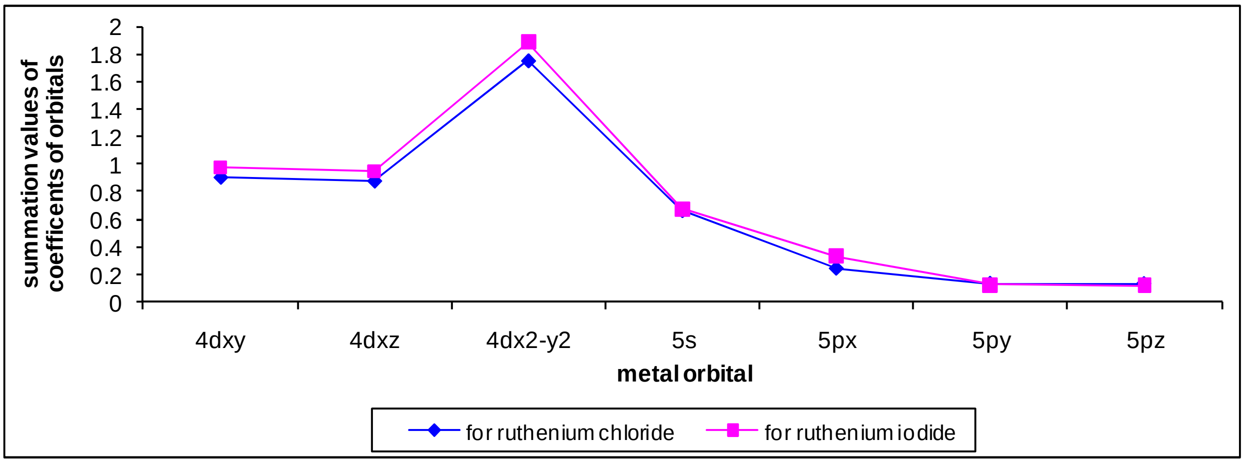

Fig- 2 Trend of extent of involvement of metal orbital in the formation of MOs of $RuCl_2$ & RuI_2

3.1. Population Analysis:

The contributions of electrons in each occupied MO are calculated by using the population analysis method, introduced by Mulliken. This method apportions the electrons of n-electron molecule into net population n_r in the basis function χ_r.

Let there be n_i electrons in the MO ϕ_i (n_i = 0, 1, 2) and let $n_{r,i}$ symbolize the contribution of electrons in the MO ϕ_i to the net population in χ_r. We have

$$n_{r,i} = n_i \, c_{ri}^2 \qquad (1)$$

where, c_{ri} is the coefficient of atomic orbitals for the ith MO (r =1–17).

Equation- 1 has been solved for 22 electrons of 11 molecular orbitals. Two electrons in the Ist MO to 11th MO have been considered. The six molecular orbitals having no electron are left over. The data relating to c_{ri} have been taken from Table 1.1, 1.2. The results of solution of equation-1 are included in Table 3.1, 3.2 which enlists the contribution of electrons in molecular orbitals under two sections- major and minor. It is evident that major contribution is from 4d and 5s orbital. The p orbitals have negligible contribution. The details of contribution are as below:

Table 3.1: Contribution of electrons in MO of Ruthenium (II) chloride.

MO. No	n_i	Major contribution		Minor contribution	
		Basis function (χ_r)	$n_{r,i} = n_i c^2_{ri}$	Basis function (χ_r)	$n_{r,i} = n_i c^2_{ri}$
1	2	5s (Ru 1)	0.0211	$4dz^2$ (Ru 1)	0.0073
		$4dx^2$-y^2 (Ru 1)	0.0220		
		3s (Cl 2)	0.8780		
		3s (Cl 3)	0.8780		
2	2	3s (Cl 2)	0.9327	5px (Ru 1)	0.0094
		3s (Cl 3)	0.9327		
3	2	$4dx^2$-y^2 (Ru 1)	0.4283	5s (Ru 1)	0.0186
		$4dz^2$ (Ru 1)	0.1428	3s (Cl 2)	0.0494
		3px (Cl 2)	0.4833	3s (Cl 3)	0.0494
		3px (Cl 3)	0.4833		
4	2	4dxz (Ru 1)	1.0999	4dxy (Ru 1)	0.0304
		3pz (Cl 2)	0.3147	4py (Cl 2)	0.0087
		3pz (Cl 3)	0.3147	4py (Cl 3)	0.0087
5	2	4dxy (Ru 1)	1.0996	4dxz (Ru 1)	0.0304
		3py (Cl 2)	0.3145	3pz (Cl 2)	0.0087
		3py (Cl 3)	0.3145	3pz (Cl 3)	0.0087
6	2	4dyz (Ru 1)	1.9996		
7	2	$4dx^2$-y^2 (Ru 1)	0.4998		
		$4dz^2$ (Ru 1)	1.4999		
8	2	5px (Ru 1)	0.0565	3s (Cl 2)	0.0091
		3px (Cl 2)	0.8199	3s (Cl 3)	0.0091
		3px (Cl 3)	0.8199		
9	2	5py (Ru 1)	0.0323		
		3py (Cl 2)	0.9237		
		3py (Cl 3)	0.9237		
10	2	5pz (Ru 1)	0.0323		
		3pz (Cl 2)	0.9237		
		3pz (Cl 3)	0.9237		
11	2	5s (Ru 1)	0.4237		
		$4dx^2$-y^2 (Ru 1)	0.8895		
		$4dz^2$ (Ru 1)	0.2866		
		3px (Cl 2)	0.1581		
		3px (Cl 3)	0.1581		

Besides contribution of electrons the Mulliken's method is also used for evaluating overlap population, in order to distinguish bonding, nonbonding and antibonding molecular orbitals. This method allocates proportionally the overlap population n_{r-s} for all possible pairs of basis functions. Which is shown by the equation-2.

$$n_{r-s,i} = n_i\,(2c_{ri}\,c_{si}\,S_{rs}) \qquad (2)$$

Where, c_{ri} = the coefficient of atomic orbitals for one atom.

c_{si} = the coefficient of atomic orbitals for other atom
and S_{rs} = the overlap integral between the two AOs (one of an atom and one of other atom).

Table 3.2: Overlap populations of Ist MO of Ruthenium (II) iodide.

n_i	AOs	c_{ri}	AOs	c_{si}	S_{rs}	$n_{r\text{-}s,i} = n_i(2c_{ri}.c_{si}.S_{rs})$
2	5s(Ru 1)	0.1682	5s(I 2)	0.6043	0.1844	0.0749
2	5s(Ru 1)	0.1682	5px(I 2)	-0.0470	-0.2793	0.0088
2	5s(Ru 1)	0.1682	5py(I 2)	-0.0005	-0.0030	0.0000
2	5s(Ru 1)	0.1682	5s(I 3)	0.6043	0.1844	0.0749
2	5s(Ru 1)	0.1682	5px(I 3)	0.0470	0.2793	0.0088
2	5s(Ru 1)	0.1682	5py(I 3)	0.0005	0.0030	0.0000
2	$4dx^2$-y^2(Ru 1)	0.2522	5s(I 2)	0.6043	0.0748	0.0455
2	$4dx^2$-y^2(Ru 1)	0.2522	5px(I 2)	-0.0470	-0.1156	0.0054
2	$4dx^2$-y^2(Ru 1)	0.2522	5py(I 2)	-0.0005	-0.0026	0.0000
2	$4dx^2$-y^2(Ru 1)	0.2522	5s(I 3)	0.6043	0.0748	0.0455
2	$4dx^2$-y^2(Ru 1)	0.2522	5px(I 3)	0.0470	0.1156	0.0054
2	$4dx^2$-y^2(Ru 1)	0.2522	5py(I 3)	0.0005	0.0026	0.0000
2	$4dz^2$(Ru 1)	-0.1457	5s(I 2)	0.6043	-0.0432	0.0152
2	$4dz^2$(Ru 1)	-0.1457	5px(I 2)	-0.0470	0.0667	0.0018
2	$4dz^2$(Ru 1)	-0.1457	5py(I 2)	-0.0005	0.0007	0.0000
2	$4dz^2$(Ru 1)	-0.1457	5s(I 3)	0.6043	-0.0432	0.0152
2	$4dz^2$(Ru 1)	-0.1457	5px(I 3)	0.0470	-0.0667	0.0018
2	$4dz^2$(Ru 1)	-0.1457	5py(I 3)	0.0005	-0.0007	0.0000
2	4dxy(Ru 1)	0.0055	5s(I 2)	0.6043	0.0016	0.0000
2	4dxy(Ru 1)	0.0055	5px(I 2)	-0.0470	-0.0032	0.0000
2	4dxy(Ru 1)	0.0055	5py(I 2)	-0.0005	0.0605	0.0000
2	4dxy(Ru 1)	0.0055	5s(I 3)	0.6043	0.0016	0.0000
2	4dxy(Ru 1)	0.0055	5px(I 3)	0.0470	0.0032	0.0000
2	4dxy(Ru 1)	0.0055	5py(I 3)	0.0005	-0.0605	0.0000
2	5s(I 2)	0.6043	5s(I 3)	0.6043	0.0001	0.0001
2	5s(I 2)	0.6043	5px(I 3)	0.0470	0.0006	0.0000
2	5px(I 2)	-0.0470	5s(I 3)	0.6043	-0.0006	0.0000
2	5px(I 2)	-0.0470	5px(I 3)	0.0470	-0.0024	0.0000
2	5py(I 2)	-0.0005	5py(I 3)	0.0005	0.0002	0.0000
						$\sum n_{r\text{-}s,i} = 0.3033$

It is evident from equation-2 that for overlap population analysis of MOs of a molecule, we need eigenvector values (coefficients), values of overlap matrix (overlap integrals) and number of electrons in each MO. The eigenvector and overlap integral values for halides of ruthenium have been taken from Table-1.1, 1.2 and Table-2.1, 2.2 respectively and the number of electrons is taken as two for Ist to 11th MOs and zero for 12th to 17th MO. With these values Table 4 is constructed for overlap-population contributions $n_{r\text{-}s,i}$ of one molecular orbital. This table has 7 columns, defined as below. There will be 17 such tables for 17 MO but only 11 tables for each halide are constructed, because remaining six which have no electrons are left over. In such a way there will be 22 tables for all the two halides.

Column 1 – number of electron n_i
Column 2, 4 – atomic orbitals of ruthenium and halogen.
Column 3 – coefficients of AOs of one atom (c_{ri})
Column 5 – coefficients of AOs of other atom (c_{si})

Column 6 – overlap integral between two AOs of different atoms (S_{rs})
Column 7 – overlap population contribution $n_{r-s,i}$.

The possible overlaps between the various AOs of metal and halogens in each molecular orbital will be 88, as detailed below–
8 overlaps – 5s AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 5px AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 5py AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 5pz AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – $4dx^2–y^2$ AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – $4dz^2$ AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 4dxy AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 4dxz AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
8 overlaps – 4dyz AO of ruthenium with ns, npx, npy, npz AOs of X-2 and X-3.
4 overlaps – ns AO of X–2 with ns, npx, npy, npz AO of X-3.
4 overlaps – npx AO of X–2 with ns, npx, npy, npz AO of X-3.
4 overlaps – npy AO of X–2 with ns, npx, npy, npz AO of X-3.
4 overlaps – npz AO of X–2 with ns, npx, npy, npz AO of X-3.
Total– 88 overlaps

For the study of overlap population we have to construct eleven tables for each halide, each having 88 possible overlaps but while building up the table we have dropped the values of zero eigenvector value (Table 1.1, 1.2), hence each table of overlap-population contribution differs in its number of orbitals. For obtaining the values of overlap-population contributions ($n_{r-s,i}$) we have to discuss each table separately, but for brevity we here discuss Table 4 for Ist MO of ruthenium chloride.

Ruthenium chloride:
This table has 31 possible overlaps; out of which 24 provide coefficient values of ruthenium orbitals and 7 for Cl-2, in column 3 that are c_{ri}. Column-5 is for coefficient value c_{si}, for both the chlorines. Up to 24, both the chlorines are involved and for remaining seven only Cl-3. Column-6 is overlapping integral S_{rs} and exhibits the magnitude of overlap between the AOs represented in column-2 and 4. The values are self explanatory for indicating the magnitude.

Ruthenium iodide
This table has 29 possible overlaps; out of which 24 provide coefficient values of ruthenium orbitals and 5 for I-2, in column 3 that are c_{ri}. Column-5 is for coefficient value c_{si}, for both the chlorines. Up to 24, both the iodides are involved and for remaining five only I-3. Column-6, is overlap integral S_{rs} and exhibits the magnitude of overlap between the AOs represented in column-2 and 4. The values are self explanatory for indicating the magnitude.

The overlap population analysis also shows negligible involvement of 5p orbitals of ruthenium. It has earlier been suggested that much smaller radius of the 4d orbital than the 5s orbital makes the involvement of 5s orbital dominant contribution in the bonding [22, 23]. This hypothesis is the central theme of a recent text book of transition-metal chemistry by Gerloch and Constable [24]. While the importance of the valence ns and (n-1) d functions for the description for transition metal bond is undisputed, the status of the empty np orbital is controversially discussed.

Table 4: Overlap populations of Ist MO of Ruthenium (II) chloride.

n_i	AOs	c_{ri}	AOs	c_{si}	S_{rs}	$n_{r\text{-}s,i} = n_i(2c_{ri}.c_{si}.S_{rs})$
2	5s(Ru 1)	-0.1029	3s(Cl 2)	-0.6626	0.2270	0.06190
2	5s(Ru 1)	-0.1029	3px(Cl 2)	-0.0142	-0.3205	-0.00187
2	5s(Ru 1)	-0.1029	3py(Cl 2)	-0.0002	-0.0035	0.00000
2	5s(Ru 1)	-0.1029	3s(Cl 3)	-0.6626	0.2270	0.06190
2	5s(Ru 1)	-0.1029	3px(Cl 3)	0.0142	0.3205	-0.00187
2	5s(Ru 1)	-0.1029	3py(Cl 3)	0.0002	0.0035	0.00000
2	$4dx^2\text{-}y^2$(Ru 1)	-0.1049	3s(Cl 2)	-0.6626	0.0994	0.02763
2	$4dx^2\text{-}y^2$(Ru 1)	-0.1049	3px(Cl 2)	-0.0142	-0.1310	-0.00078
2	$4dx^2\text{-}y^2$(Ru 1)	-0.1049	3py(Cl 2)	-0.0002	-0.0034	0.00000
2	$4dx^2\text{-}y^2$(Ru 1)	-0.1049	3s(Cl 3)	-0.6626	0.0994	0.02763
2	$4dx^2\text{-}y^2$(Ru 1)	-0.1049	3px(Cl 3)	0.0142	0.1310	-0.00078
2	$4dx^2\text{-}y^2$(Ru 1)	-0.1049	3py(Cl 3)	0.0002	0.0034	0.00000
2	$4dz^2$(Ru 1)	0.0606	3s(Cl 2)	-0.6626	-0.0574	0.00921
2	$4dz^2$(Ru 1)	0.0606	3px(Cl 2)	-0.0142	0.0757	-0.00026
2	$4dz^2$(Ru 1)	0.0606	3py(Cl 2)	-0.0002	0.0008	0.00000
2	$4dz^2$(Ru 1)	0.0606	3s(Cl 3)	-0.6626	-0.0574	0.00921
2	$4dz^2$(Ru 1)	0.0606	3px(Cl 3)	0.0142	-0.0757	-0.00026
2	$4dz^2$(Ru 1)	0.0606	3py(Cl 3)	0.0002	-0.0008	0.00000
2	4dxy(Ru 1)	-0.0023	3s(Cl 2)	-0.6626	0.0022	0.00001
2	4dxy(Ru 1)	-0.0023	3px(Cl 2)	-0.0142	-0.0038	0.00000
2	4dxy(Ru 1)	-0.0023	3py(Cl 2)	-0.0002	0.0923	0.00000
2	4dxy(Ru 1)	-0.0023	3s(Cl 3)	-0.6626	0.0022	0.00001
2	4dxy(Ru 1)	-0.0023	3px(Cl 3)	0.0142	0.0038	0.00000
2	4dxy(Ru 1)	-0.0023	3py(Cl 3)	0.0002	-0.0923	0.00000
2	3s(Cl 2)	-0.6626	3s(Cl 3)	-0.6626	0.0004	0.00070
2	3s(Cl 2)	-0.6626	3px(Cl 3)	0.0142	0.0027	-0.00010
2	3px(Cl 2)	-0.0142	3s(Cl 3)	-0.6626	-0.0027	-0.00010
2	3px(Cl 2)	-0.0142	3px(Cl 3)	0.0142	-0.0108	0.00000
2	3px(Cl 2)	-0.0142	3py(Cl 3)	0.0002	-0.0001	0.00000
2	3py(Cl 2)	-0.0002	3px(Cl 3)	0.0142	-0.0001	0.00000
2	3py(Cl 2)	-0.0002	3py(Cl 3)	0.0002	0.0011	0.00000
						$\sum n_{r\text{-}s,i} = 0.19218$

Our results indicate that involvement of np orbital in transition metal bond is negligible and the main role is played by ns and by (n-1) d orbital. Landis [1-3] has also emphatically denied the involvement of np orbital in hybridization. He has supported sd hybridization and has based his observation on the bond angles. The idealized sd hybridization has been shown to have angles of 90^0 .This is because the energy curves are a function of the bond angles and have two minima one below 90^0 and one above 90^0. The bond angles also support the Landis concept.

The column-7 of Table 4 enlists the values of overlap population, derived from the equation –2. The sum of the values of overlap-populations decides whether the MO in a covalent molecule is bonding, nonbonding or antibonding. If the sum of this inter atomic overlap population contribution is substantially positive, the MO is bonding; if substantially negative, the MO is antibonding and if zero or near zero, the MO is nonbonding. Table 4 indicates that the sum of overlap- population contribution in first MO of $RuCl_2$ is 0.19218 which is positive indicating or supporting the bonding nature of MO.

Similarly the sum of overlap population for the 11 MO in each halide has been worked out and the results are tabulated in Table 5 below:

Table 5			
Nature of occupied MOs of $RuCl_2$			
MO. No	Sum of overlap population contribution ($\sum n_{r\text{-}s,I}$)		Nature of MOs
1	0.19218	Positive	Bonding
2	0.12479	Positive	Bonding
3	0.22345	Positive	Bonding
4	0.22263	Positive	Bonding
5	-0.21482	Negative	Antibonding
6	0.00000	Zero	Nonbonding
7	0.00000	Zero	Nonbonding
8	0.28493	Positive	Bonding
9	0.06038	Positive	Bonding
10	0.12005	Positive	Bonding
11	0.07327	Positive	Bonding
Nature of occupied MOs of RuI_2			
1	0.3033	Positive	Bonding
2	0.0888	Positive	Bonding
3	0.0934	Positive	Bonding
4	0.0934	Positive	Bonding
5	0.1329	Positive	Bonding
6	0.00000	Zero	Nonbonding
7	0.00000	Zero	Nonbonding
8	0.3358	Positive	Bonding
9	0.3062	Positive	Bonding
10	0.0781	Positive	Bonding
11	0.0781	Positive	Bonding

The overlap population analysis as presented in Table 5 shows that the nonbonding electrons are present in 6^{th} and 7^{th} molecular orbitals in both $RuCl_2$ and RuI_2. The non bonding orbital is degenerate in all the cases. The eigenvector analysis as presented in Table-1.1, 1.2 indicates that these orbitals are 4dyz and $4dz^2$.

From the above discussion it is clear that no molecular orbital is formed by only two atomic orbitals. All molecular orbitals have contribution of many basis functions or atomic orbitals; as a result every molecular orbital has a definite shape having contribution from many basis functions.

CONCLUSION

- Eigenvector analysis shows that $4dx^2\text{-}y^2$ and 4dxy orbitals of ruthenium play a major role in bonding between ruthenium and halides, 5s orbital is next and 4p orbitals have a negligible role. This supports the Landis observation and concept of sd hybridization.
- s and p orbitals of halogen are involved in bonding with ruthenium. There is a difference in energy levels of s and p orbitals are 0.1691 in chloride and 0.7472 in iodide.

- The overlap population analysis shows that the nonbonding orbitals are present in 6^{th} and 7^{th} molecular orbitals in both.
- No molecular orbital is formed by only two atomic orbitals. All molecular orbitals have contribution from many atomic orbitals; the difference is only in extent of involvement.

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