sd-Hybridization, Population Analysis and MOT in Ru^{2+}.II. Ruthenium mixeddihalides

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Abstract: As we know that chloride, bromide and iodide have different positions in nephelauxetic and electrochemical series. These points make us to study ruthenium mixedhalides in the same manner as the simple ruthenium dihalides. A quantitative atomic orbital (AO) and molecular orbital (MO) treatment has been made on ruthenium(II) mixedhalides: Br—Ru—Cl, I—Ru—Br, and I—Ru—Cl. The $\sum c_i$ values of metal's AOs: $4dx^2$-y^2, 4dxz, 4dxy, 5s, 5px, 5py, 5pzin their mixeddihalides show sd-hybridization. Further, $\sum c_i$ values are highest in case of Ru(II)ICl and lowest in Ru(II)BrCl. This is due to cloud expending of halides.The value of magnitude of splitting of metal d orbital is highest in Ru(II)BrCl and lowest in Ru(II)IBr. This is due to dominancy to one atom that has priority in electrochemical series to the other atom. The study concluded that all the MOs ($\phi_1 - \phi_{17}$) have definite energy and definite shape due to different contribution of many basis functions ($\chi_1 - \chi_{17}$), difference in energies of overlapping AOs and their symmetry (phase). In Br—Ru—Cl and I—Ru—B, the bonding molecular orbitals are $\phi_1 - \phi_5$ and $\phi_8 - \phi_{11}$, nonbonding molecular orbital are ϕ_6 and ϕ_7. In I—Ru—Cl bonding molecular orbitals are $\phi_1 - \phi_5$, ϕ_8 and ϕ_{11}, nonbonding molecular orbital are ϕ_6 and ϕ_7, which are purely two d atomic orbitals of ruthenium namely dxz and dz^2, and remaining two ϕ_9 and ϕ_{10} are antibonding. The study at a glance provides clear cut electronic picture of the molecule, which more precisely can explain or help to explain the various properties of the complex compounds synthesized by these molecules, which may be a requisite for the synthesis of various ruthenium(II) complex compounds.
Key-words: Ruthenium mixeddihalides, Atomic orbital treatment, Molecular orbital treatment and Mulliken population analysis.

I.   INTRODUCTION

Three mixeddihalides are possible for ruthenium viz., Br−Ru−Cl (1st), Br−Ru−I (2nd) and Cl−Ru−I (3rd). If we compare the constituents of 1st and 2ndmixeddihalides then we found that left arms of Ru in both the mixed halides are same, while the right arms are different. These arms just represent the halves of the Cl−Ru−Cl and I−Ru−I that is Ru−Cl and Ru−I, respectively. In the same manner, if we compare between the 2nd and 3rdmixeddihalides then we find that their right arms are same but their left arms differ and match with halves arms of the Br−Ru−Br and Cl−Ru−Cl that is Br−Ru and Cl−Ru, respectively (Scheme-1).
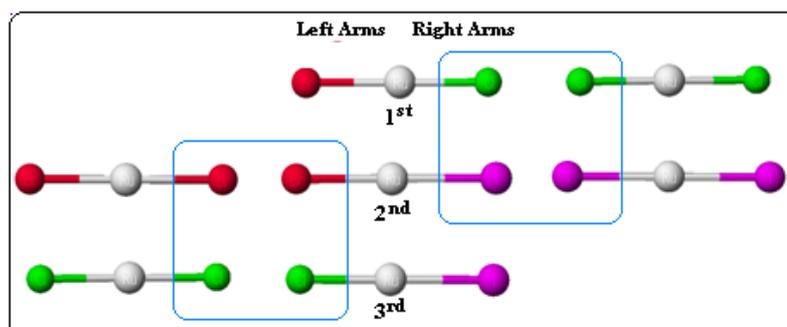
Scheme 1. Similarities and dissimilarities among simple and mixeddihalides

As we know that chloride, bromide and iodide have different positions in nephelauxetic and electrochemical series. These points make us to study these ruthenium mixedhalides in the same manner as the simple ruthenium dihalides.

II. MATERIALS AND METHODS

The study materials of this research work are Ru(II)BrCl, Ru(II)IBr and Ru(II)ICl.The 3D modeling and geometry optimization of the halides have also been made by adopting same procedure and same methods as in case of simple ruthenium(II) halides. Eigenvectors,overlap matrix and eigenvalues have been computed with the same software, using the same option. The method adopted for various calculations are based on Mulliken population analysis (MPA) [1, 2]. Within the LCAO-MO approximation, the wave function for i^{th} eigenstate of molecule as defined by Mulliken is

$$\phi_i = \sum_{rk} c_{irk} \chi_{rk} \qquad \text{Eq. 1}$$

The contributions of electrons ($n_{r,i}$) in each occupied MO are calculated by using the following as proposed by Mulliken

$$n_{r,i} = n_i c_{ri}^2 \qquad \text{Eq. 2}$$

where n_i is the number of electron in MO ϕ_i and c_{ri} is the coefficient of AOs for MO ϕ_i ($i = 1-17$). Thereafter, MPA has also used for evaluating overlap population as described below

$$n_{r-s,i} = n_i (2c_{ri} c_{si} S_{rs}) \qquad \text{Eq. 3}$$

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

III. RESULTS AND DISCUSSION

A systematic molecular mechanics based investigation of bonding nature in ruthenium(II)mixeddihalides has been studied. Mixeddihalides, which are under investigation, are: RuBrCl, RuIBr and RuICl.

3.1 Ruthenium(II)BrCl

Ruthenium(II)BrCl is triatomic molecule, having the following optimized geometry as obtained from molecular mechanics method.

Br—Ru, Bond Length = 2.389Å
Ru—Cl, Bond Length = 2.239Å
Bond Angle =179.99°

Fig. 1 Structure of Ru(II)BrCl

The MOs of this molecule are formed by linear combination 17 AOs of nine orbitals (five 4d-orbitals, one 5s orbital and three 5p orbitals) from ruthenium and four orbitals (one 4s orbital and three 4p orbitals) from bromine and four orbitals (one 3s orbital and three 5p orbitals) chlorine atom. These are χ_1–χ_9 are atomic orbitals of ruthenium, χ_{10}–χ_{13} of bromine and χ_{14}–χ_{17} are atomic orbitals of chlorine: (χ_1 = 5s, χ_2 = 5px, χ_3 = 5py, χ_4 = 5pz, χ_5 = 4dx²-y², χ_6 = 4dz², χ_7 = 4dxy, χ_8 = 4dxz, χ_9 = 4dyz, for Ru-1 and χ_{10} = 4s, χ_{11} = 4px, χ_{12} = 4py, χ_{13} = 4pz for I-2 and χ_{14} = 3s, χ_{15} = 3px, χ_{16} = 3py, χ_{17} = 3pz for Cl-3). These 17 AOs on LCAO approximations give 17 MOs (represented by ϕ_1 to ϕ_{17}). The magnitude of contribution of various AOs (χ) in the formation of 17 MOs is demonstrated by Eqs., ϕ_1 to ϕ_{17}. Here, the coefficients of χ are the eigenvector and its zero or near zero values have been omitted.

ϕ_1 = -0.0772χ_1 +0.0447χ_2 +0.0039χ_3 -0.0773χ_5 +0.0453χ_6 -0.0135χ_7 -0.0221χ_{10} 0.0002χ_{11} -0.9501χ_{14} +0.0226χ_{15} +0.0020χ_{16}

ϕ_2 = -0.0829χ_1 -0.0652χ_2 -0.0057χ_3 -0.0962χ_5 +0.0564χ_6 -0.0169χ_7 -0.9416χ_{10} -0.0138χ_{11} -0.0012χ_{12} +0.0548χ_{14} -0.0179χ_{15} -0.0016χ_{16}

ϕ_3 = 0.0804χ_1 -0.0180χ_2 -0.0016χ_3 +0.4929χ_5 -0.2889χ_6 +0.0864χ_7 -0.1771χ_{10} -0.3026χ_{11} -0.0263χ_{12} -0.1657χ_{14} +0.5942χ_{15} +0.0517χ_{16}

ϕ_4 = -0.0217χ_4 +0.0001χ_5 -0.0005χ_7 +0.7803χ_8 +0.0679χ_9 -0.0001χ_{12} +0.1964χ_{13} +0.0003χ_{16} -0.5000χ_{17}

ϕ_5 = 0.0019χ_2 -0.0216χ_3 -0.1352χ_5 +0.7715χ_7 +0.0005χ_8 -0.0170χ_{11} +0.1957χ_{12} +0.0001χ_{13} +0.0433χ_{15} -0.4981χ_{16} -0.0003χ_{17}

ϕ_6 = -0.0866χ_8 +0.9962χ_9

ϕ_7 = 0.4925χ_5 +0.8660χ_6 +0.0863χ_7

ϕ_8 = -0.1710χ_1 +0.1607χ_2 +0.0140χ_3 +0.3627χ_5 -0.2126χ_6 +0.0636χ_7 -0.1010χ_{10} -0.5121χ_{11} -0.0445χ_{12} +0.0357χ_{14} -0.6037χ_{15} -0.0525χ_{16}

ϕ_9 = -0.0106χ_2 +0.1222χ_3 -0.0641χ_5 +0.3659χ_7 -0.0001χ_8 -0.0442χ_{11} +0.5086χ_{12} -0.0001χ_{13} -0.0649χ_{15} +0.7463χ_{16} -0.0002χ_{17}

ϕ_{10} = 0.1227χ_4 +0.0001χ_7 +0.3701χ_8 +0.0322χ_9 +0.0001χ_{12} +0.5105χ_{13} +0.0002χ_{16} +0.7491χ_{17}

ϕ_{11} = -0.4464χ_1 -0.0847χ_2 -0.0074χ_3 +0.5151χ_5 -0.3019χ_6 +0.0903χ_7 +0.0563χ_{10} +0.5808χ_{11} +0.0505χ_{12} -0.0086χ_{14} -0.0665χ_{15} -0.0058χ_{16}

ϕ_{12} = 0.0266χ_4 +0.0001χ_5 -0.0004χ_7 -0.5101χ_8 -0.0444χ_9 -0.0001χ_{11} +0.0006χ_{12} +0.8231χ_{13} -0.0003χ_{16} -0.3960χ_{17}

ϕ_{13} = 0.0023χ_2 -0.0265χ_3 -0.0884χ_5 +0.5044χ_7 -0.0004χ_8 +0.0713χ_{11} -0.8200χ_{12} +0.0006χ_{13} -0.0343χ_{15} +0.3945χ_{16} -0.0003χ_{17}

ϕ_{14} = 0.0881χ_2 -1.0130χ_3 +0.0007χ_4 -0.0036χ_5 +0.0206χ_7 -0.0190χ_{11} +0.2182χ_{12} -0.0002χ_{13} -0.0232χ_{15} +0.2669χ_{16} -0.0002χ_{17}

ϕ_{15} = -0.0001χ_2 +0.0007χ_3 +1.0169χ_4 -0.0208χ_8 -0.0018χ_9 -0.0002χ_{12} -0.2190χ_{13} -0.0002χ_{16} -0.2679χ_{17}

ϕ_{16} = 1.0384χ_1 +0.2909χ_2 +0.0253χ_3 +0.3663χ_5 -0.2147χ_6 +0.0642χ_7 -0.4169χ_{10} +0.7037χ_{11} +0.0612χ_{12} -0.2425χ_{14} -0.4512χ_{15} -0.0392χ_{16}

ϕ_{17} = 0.3062χ_1 -1.3663χ_2 -0.1188χ_3 +0.1121χ_5 -0.0657χ_6 +0.0196χ_7 +0.3630χ_{10} -0.4675χ_{11} -0.0406χ_{12} -0.5994χ_{14} -0.7660χ_{15} -0.0666χ_{16}

3.2 Ruthenium(II)IBr

Ru(II)IBr is also triatomic molecule having the following optimized geometry as obtained from molecular mechanics method.

I—Ru, Bond Length = 2.579Å
Ru—Br, Bond Length = 2.389Å
Bond Angle =179.99°

Fig. 2 Structure of Ru(II)IBr

The MOs of this molecule as formed by linear combination of 17 AOs (χ_1–$\chi17$), where χ_1 = 5s, χ_2 = 5px, χ_3 = 5py, χ_4 = 5pz, χ_5 = 4dx^2-y^2, χ_6 = 4dz^2, χ_7 = 4dxy, χ_8 = 4dxz, χ_9 = 4dyz, for Ru-1 and χ_{10} = 5s, χ_{11} = 5px, χ_{12} = 5py, χ_{13} = 5pz for I-2 and χ_{14} = 4s, χ_{15} = 4px, χ_{16} = 4py, χ_{17} = 4pz for Br-3. These 17 AOs on LCAO approximations give 17 MOs (represented by ϕ_1 to ϕ_{17}). The magnitude of contribution of various AOs (χ) in the formation of 17 MOs is demonstrated by Eqs., ϕ_1 to ϕ_{17}. Here, the coefficients of χ are the eigenvector and its zero or near zero values have been omitted.

ϕ_1 = -0.0935χ_1 +0.0562χ_2 +0.0049χ_3 -0.1065χ_5 +0.0624χ_6 -0.0187χ_7 -0.0281χ_{10} +0.0091χ_{11} +0.0008χ_{12} -0.9397χ_{14} +0.0122χ_{15} +0.0011χ_{16}

ϕ_2 = 0.1153χ_1 +0.0876χ_2 +0.0076χ_3 +0.1794χ_5 -0.1051χ_6 +0.0314χ_7 +0.8955χ_{10} -0.0300χ_{11} -0.0026χ_{12} -0.0915χ_{14} +0.0547χ_{15} +0.0048χ_{16}

ϕ_3 = 0.0172χ_1 -0.0153χ_2 -0.0013χ_3 +0.5939χ_5 -0.3481χ_6 +0.1041χ_7 -0.3054χ_{10} -0.3194χ_{11} -0.0278χ_{12} -0.1859χ_{14} +0.4354χ_{15} +0.0379χ_{16}

ϕ_4 = 0.0054χ_4 -0.0001χ_7 -0.9021χ_8 -0.0784χ_9 -0.1928χ_{13} +0.2886χ_{17}

ϕ_5 = -0.0005χ_2 +0.0053χ_3 +0.1563χ_5 -0.8920χ_7 +0.0001χ_8 +0.0167χ_{11} -0.1921χ_{12} -0.0250χ_{15} +0.2875χ_{16}

ϕ_6 = -0.0866χ_8 +0.9962χ_9

ϕ_7 = 0.4925χ_5 +0.8660χ_6 +0.0863χ_7

ϕ_8 = 0.1622χ_1 -0.1897χ_2 -0.0165χ_3 -0.2275χ_5 +0.1334χ_6 -0.0399χ_7 +0.0972χ_{10} +0.4800χ_{11} +0.0417χ_{12} -0.0753χ_{14} +0.6839χ_{15} +0.0595χ_{16}

ϕ_9 = -0.4711χ_1 -0.0689χ_2 -0.0060χ_3 +0.4677χ_5 -0.2741χ_6 +0.0820χ_7 +0.0913χ_{10} +0.5806χ_{11} +0.0505χ_{12} +0.0137χ_{14} -0.1646χ_{15} -0.0143χ_{16}

ϕ_{10} = -0.0001χ_3 +0.1211χ_4 -0.0001χ_7 +0.1638χ_8 +0.0142χ_9 -0.0004χ_{12} +0.5355χ_{13} -0.0006χ_{16} +0.7988χ_{17}

$\phi_{11} = 0.0105\chi_2 - 0.1207\chi_3 - 0.0001\chi_4 + 0.0284\chi_5 - 0.1619\chi_7 - 0.0001\chi_8 + 0.0464\chi_{11} - 0.5335\chi_{12} - 0.0004\chi_{13} + 0.0692\chi_{15} - 0.7958\chi_{16} - 0.0006\chi_{17}$

$\phi_{12} = 0.0198\chi_4 + 0.0002\chi_7 - 0.4009\chi_8 - 0.0349\chi_9 - 0.0003\chi_{12} + 0.8087\chi_{13} + 0.0002\chi_{16} - 0.5017\chi_{17}$

$\phi_{13} = -0.0017\chi_2 + 0.0197\chi_3 + 0.0695\chi_5 - 0.3964\chi_7 - 0.0002\chi_8 - 0.0701\chi_{11} + 0.8057\chi_{12} + 0.0003\chi_{13} + 0.0435\chi_{15} - 0.4998\chi_{16} - 0.0002\chi_{17}$

$\phi_{14} = -0.0064\chi_2 + 0.0742\chi_3 - 1.0065\chi_4 + 0.0001\chi_5 - 0.0007\chi_7 + 0.0098\chi_8 + 0.0009\chi_9 + 0.0013\chi_{11} - 0.0147\chi_{12} + 0.2000\chi_{13} + 0.0015\chi_{15} - 0.0167\chi_{16} + 0.2265\chi_{17}$

$\phi_{15} = 0.0872\chi_2 - 1.0027\chi_3 - 0.0744\chi_4 - 0.0017\chi_5 + 0.0097\chi_7 + 0.0007\chi_8 + 0.0001\chi_9 - 0.0173\chi_{11} + 0.1993\chi_{12} + 0.0148\chi_{13} - 0.0196\chi_{15} + 0.2257\chi_{16} + 0.0168\chi_{17}$

$\phi_{16} = -1.0203\chi_1 - 0.1233\chi_2 - 0.0107\chi_3 - 0.3396\chi_5 + 0.1990\chi_6 - 0.0595\chi_7 + 0.3637\chi_{10} - 0.6373\chi_{11} - 0.0554\chi_{12} + 0.2740\chi_{14} + 0.5217\chi_{15} + 0.0454\chi_{16}$

$\phi_{17} = -0.1217\chi_1 + 1.3166\chi_2 + 0.1145\chi_3 - 0.0554\chi_5 + 0.0325\chi_6 - 0.0097\chi_7 - 0.3867\chi_{10} + 0.5408\chi_{11} + 0.0470\chi_{12} + 0.4764\chi_{14} + 0.6643\chi_{15} + 0.0578\chi_{16}$

3.3 Ruthenium(II)ICl

The optimized geometry of Ru(II)ICl as obtained from molecular mechanics method is shown below.

I—Ru, Bond Length = 2.579Å
Ru—Cl Bond Length = 2.239Å
Bond Angle =179.99°

Fig.3 Structure of Ru(II)ICl

The MOs of this molecule as formed by linear combination 17 AOs (χ_1–χ_{17}), where $\chi_1 = 5s$, $\chi_2 = 5px$, $\chi_3 = 5py$, $\chi_4 = 5pz$, $\chi_5 = 4dx^2$-y^2, $\chi_6 = 4dz^2$, $\chi_7 = 4dxy$, $\chi_8 = 4dxz$, $\chi_9 = 4dyz$, for Ru-1 and $\chi_{10} = 5s$, $\chi_{11} = 5px$, $\chi_{12} = 5py$, $\chi_{13} = 5pz$ for I-2 and $\chi_{14} = 3s$, $\chi_{15} = 3px$, $\chi_{16} = 3py$, $\chi_{17} = 3pz$ for Cl-3. These 17 AOs on LCAO approximations give 17 MOs (represented by ϕ_1 to ϕ_{17}). The magnitude of contribution of various AOs (χ) in the formation of 17 MOs is demonstrated by Eqs. ϕ_1 to ϕ_{17}. Here, the coefficients of χ are the eigenvector and its zero or near zero values have been omitted.

$\phi_1 = 0.0765\chi_1 - 0.0448\chi_2 + 0.0001\chi_3 - 0.0029\chi_4 + 0.0772\chi_5 - 0.0442\chi_6 - 0.0004\chi_7 + 0.0102\chi_8 + 0.0065\chi_{10} - 0.0001\chi_{11} + 0.9509\chi_{14} - 0.0225\chi_{15} + 0.0001\chi_{16} - 0.0015\chi_{17}$

$\phi_2 = -0.1181\chi_1 - 0.0885\chi_2 + 0.0002\chi_3 - 0.0058\chi_4 - 0.1888\chi_5 + 0.1081\chi_6 - 0.0249\chi_8 + 0.0001\chi_9 - 0.8898\chi_{10} + 0.0313\chi_{11} - 0.0001\chi_{12} + 0.0021\chi_{13} + 0.0630\chi_{14} - 0.0853\chi_{15} + 0.0002\chi_{16} - 0.0056\chi_{17}$

$\phi_3 = -0.0647\chi_1 + 0.0357\chi_2 - 0.0001\chi_3 + 0.0024\chi_4 - 0.4751\chi_5 + 0.2719\chi_6 + 0.0026\chi_7 - 0.0626\chi_8 + 0.0002\chi_9 + 0.3035\chi_{10} + 0.2312\chi_{11} - 0.0006\chi_{12} + 0.0152\chi_{13} + 0.1601\chi_{14} - 0.6259\chi_{15} + 0.0017\chi_{16} - 0.0412\chi_{17}$

$\phi_4 = 0.0001\chi_2 + 0.0261\chi_3 - 0.0044\chi_5 + 0.0002\chi_6 - 0.7834\chi_7 + 0.0013\chi_8 - 0.0516\chi_9 - 0.0516\chi_{11} - 0.1383\chi_{12} + 0.0003\chi_{13} + 0.0015\chi_{15} + 0.5210\chi_{16} - 0.0010\chi_{17}$

$\phi_5 = 0.0017\chi_2 - 0.0001\chi_3 - 0.0260\chi_4 - 0.0515\chi_5 + 0.0892\chi_6 + 0.0017\chi_7 + 0.7783\chi_8 - 0.0020\chi_9 - 0.0091\chi_{11} + 0.0003\chi_{12} + 0.1380\chi_{13} + 0.0342\chi_{15} - 0.0011\chi_{16} - 0.5198\chi_{17}$

$\phi_6 = -0.0004\chi_5 - 0.0657\chi_7 + 0.0027\chi_8 + 0.9978\chi_9$

$\phi_7 = 0.5022\chi_5 + 0.8623\chi_6 - 0.0028\chi_7 - 0.0656\chi_8 + 0.0002\chi_9$

$\phi_8 = 0.2399\chi_1 - 0.1490\chi_2 + 0.0004\chi_3 - 0.0098\chi_4 - 0.4864\chi_5 + 0.2784\chi_6 + 0.0027\chi_7 - 0.0641\chi_8 + 0.0002\chi_9 + 0.1356\chi_{10} + 0.4054\chi_{11} - 0.0011\chi_{12} + 0.0267\chi_{13} - 0.0256\chi_{14} + 0.5702\chi_{15} - 0.0016\chi_{16} + 0.0376\chi_{17}$

$\phi_9 = -0.0001\chi_2 - 0.1174\chi_3 - 0.0031\chi_4 - 0.0018\chi_5 - 0.0015\chi_6 - 0.4844\chi_7 - 0.0129\chi_8 - 0.0319\chi_9 - 0.0004\chi_{11} - 0.3817\chi_{12} - 0.0101\chi_{13} - 0.0008\chi_{15} - 0.7806\chi_{16} - 0.0207\chi_{17}$

$\phi_{10} = 0.0077\chi_2 + 0.0031\chi_3 - 0.1172\chi_4 + 0.0319\chi_5 - 0.0551\chi_6 + 0.0127\chi_7 - 0.4812\chi_8 + 0.0022\chi_9 + 0.0251\chi_{11} + 0.0101\chi_{12} - 0.3809\chi_{13} + 0.0514\chi_{15} + 0.0206\chi_{16} - 0.7789\chi_{17}$

$\phi_{11} = -0.4127\chi_1 - 0.1164\chi_2 + 0.0003\chi_3 - 0.0077\chi_4 + 0.4149\chi_5 - 0.2375\chi_6 - 0.0023\chi_7 + 0.0547\chi_8 - 0.0001\chi_9 + 0.1072\chi_{10} + 0.6763\chi_{11} - 0.0019\chi_{12} + 0.0445\chi_{13} - 0.0081\chi_{14} + 0.0095\chi_{15} + 0.0006\chi_{17}$

$\phi_{12} = 0.0001\chi_2 + 0.0371\chi_3 - 0.0002\chi_4 - 0.0024\chi_5 + 0.0003\chi_6 - 0.3982\chi_7 + 0.0025\chi_8 - 0.0262\chi_9 + 0.0029\chi_{11} + 0.9029\chi_{12} - 0.0059\chi_{13} - 0.0009\chi_{15} - 0.2922\chi_{16} + 0.0019\chi_{17}$

ϕ_{13} = 0.0024χ_2 -0.0002χ_3 -0.0370χ_4 -0.0262χ_5 +0.0453χ_6 +0.0027χ_7 +0.3957χ_8 -0.0009χ_9 +0.0593χ_{11} -0.0061χ_{12} -0.9009χ_{13} -0.0192χ_{15} +0.0020χ_{16} +0.2916χ_{17}

ϕ_{14} = 0.0426χ_2 -0.7536χ_3 -0.6780χ_4 -0.0012χ_5 +0.0023χ_6 +0.0225χ_7 +0.0202χ_8 +0.0014χ_9 -0.0082χ_{11} +0.1452χ_{12} +0.1306χ_{13} 0.0113χ_{15} +0.2004χ_{16} +0.1803χ_{17}

ϕ_{15} = -0.0514χ_2 -0.6793χ_3 +0.7519χ_4 +0.0016χ_5 -0.0026χ_6 +0.0203χ_7 -0.0224χ_8 +0.0014χ_9 +0.0099χ_{11} +0.1308χ_{12} -0.1448χ_{13} +0.0137χ_{15} +0.1806χ_{16} -0.1999χ_{17}

ϕ_{16} = -0.9976χ_1 -0.3745χ_2 -0.0247χ_4 -0.3360χ_5 +0.1923χ_6 +0.0018χ_7 -0.0443χ_8 +0.0001χ_9 +0.4347χ_{10} -0.7289χ_{11} +0.0020χ_{12} -0.0480χ_{13} +0.1959χ_{14} +0.3949χ_{15} -0.0011χ_{16} +0.0260χ_{17}

ϕ_{17} = -0.3942χ_1 +1.3256χ_2 -0.0036χ_3 +0.0873χ_4 -0.1539χ_5 +0.0881χ_6 +0.0008χ_7 -0.0203χ_8 +0.0001χ_9 -0.3082χ_{10} +0.4109χ_{11} -0.0011χ_{12} +0.0271χ_{13} +0.6133χ_{14} +0.7964χ_{15} -0.0022χ_{16} +0.0525χ_{17}

The (n-1)- and n-shells of transition metal (TM) elements play lead role to describe their properties and also boost their application in science and technology. TM elements form huge numbers of simple and complex compounds by adopting different oxidation states and coordination numbers. The complex compounds are formed either from their simple compounds or by substitution reactions from pre-synthesized complex compounds. As each compoundis collection of atoms held together by bonds. Nature of bonds and their strength alter the physical, chemical and electronic properties of the molecules and thus their applications too.

Consequence of enormous theoretical and computational developments make possible to reach just around the corner of electronic structure of the bond and finally electronic structure of the molecule, too and thus reflect the cause of alternation in the various properties of the molecule. In order to explain electronic structure of the bond and thus electronic structure of molecule, one can adopt either concept of bonded attraction and non-bonded repulsion of VB (Valence Bond) theory, and or positive and negative overlap populations of MO (Molecular Orbital) theory[3-5].

In the first case hybridization play important role that depends upon the oxidation state of TM and number and nature of combing atoms or ions, and in the second case formation of molecular orbital by LCAO approximation [6]. At first we have to examine the extent of involvement of 4d, 5s and 5p AOs of Ru-1 in the formation of MOs in ruthenium mixeddihalides. To see the total involvement of seven AOs (excluding nonbonding orbital, χ_6 and χ_7) of Ru-1 in eleven MOs(ϕ_1-ϕ_{11}), the coefficient value of each orbital has been added.

ΣAO	Ru(II)BrCl	Ru(II)IBr	Ru(II)ICl
$\Sigma 4dx2$-y2	2.4501	4.9002	9.8004
$\Sigma 4dxy$	2.1893	4.3786	8.7572
$\Sigma 4dxz$	2.1527	4.3054	8.2407
$\Sigma 5s$	1.1012	2.2024	4.4047
$\Sigma 5px$	0.7407	1.4814	2.8401
$\Sigma 5py$	0.6454	1.2908	2.5816
$\Sigma 5pz$	0.3866	0.7732	1.5464
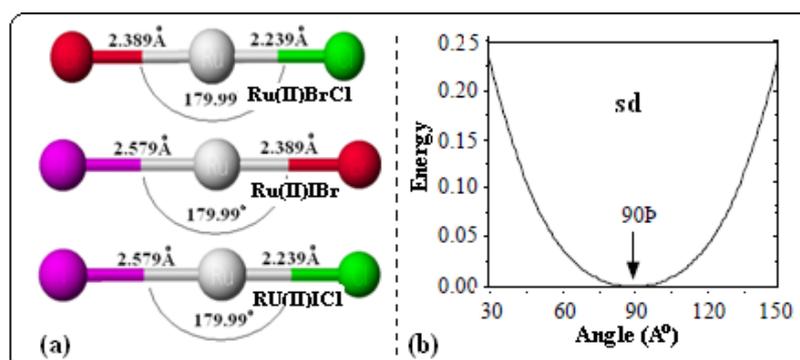
Scheme 2. (a) bond length and bond angle (b) Plot between energy and bond angle for sd-hybridization

The six vacant MOs (ϕ_{12}-ϕ_{17}) are also exempted here, as there is only 22e$^-$ to be filled by adopting Aufbau principle, Hund's rule and Pauli's exclusion principle and thus we considered only eleven MOs among the seventeen MOs. The summation values of seven AOs in these eleven MOs are given above and graphically presented for comparative study in Fig. 4, which clearly reflects maximum involvement is of 4d orbital (4dx2-y2 > 4dxz > 4dxy). Next to this is 5s orbital. The involvements of three p-orbitals are negligible as their summation value is very low in comparison to d orbital and considerably low with respect to s orbital. It is also evident from these data that the involvement of 5p orbital in Ru—X bond is insignificant and the main role is played by 5s and by 4d orbital.The bond angles as presented in Scheme-2 also grip up the Landis's model of sd^n-hybridization, when n=1 [7].
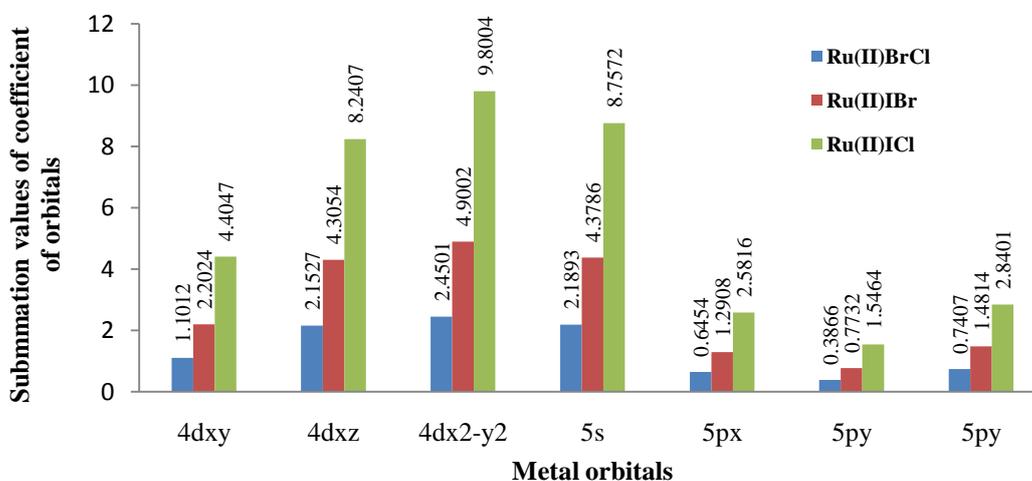
Fig. 4 Extent of involvement of metal's orbitals in ruthenium(II) mixedhalides

Further, a close look at the right side of the figure 4, very clearly demonstrated that the summation values are highest in case of Ru(II)ICl and lowest in Ru(II)BrCl. This is due to cloud expending of halides. For a given metal ion, the ability of ligands to induce this cloud expending increases according to nephelauxetic series [8]. Thus, iodide will produce greater cloud-expending effect than bromide, which intern will produce higher than chloride. In other words the effective positive charge on Ru(II) is reduced greater by iodide and lesser by chloride.But, here in each case ruthenium(II) bonded to two different halogen atoms and each halogen has its own cloud expanding effect and the trend in ruthenium mixeddihalides is Ru(II)BrCl<Ru(II)IBr<Ru(II)ICl. This can explain on the basis of electronegativity of halogens and their difference as presented below:

χ_{Cl}	χ_{Br}	χ_I	$\Delta\chi_{Cl-Br}$	$\Delta\chi_{I-Br}$	$\Delta\chi_{I-Cl}$
3.0	2.8	2.5	0.2	0.3	0.5

In, Ru(II)ICl, iodine produces greater cloud expending effect due to its lowest electronegativity among halogen. In Ru(II)IBr, the difference in electronegativity ($\Delta\chi_{I-Br}$ = 0.3) is not much lower as in case of Ru(II)ICl ($\Delta\chi_{I-Cl}$ = 0.5), hence it produces less cloud-expending effect. Ru(II)BrCl having much low difference in electronegativity ($\Delta\chi_{Cl-Br}$ =0.2) in turn produces lowest cloud-expending effect in ruthenium mixeddihalides. This can much better understand if we have a close look on Scheme-3.
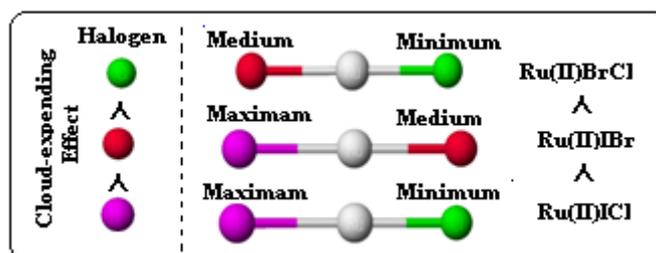
Scheme 3. Cloud expending effect of atoms in ruthenium mixeddihalides

Mulliken population analysis [2] method has been used to measure the contribution of electrons in each occupied MO. For this Eq.2 has been solved for 22e$^-$ by putting 2e$^-$ in each MO (ϕ_1-ϕ_{11}). The shape of each MO (ϕ_1-ϕ_{17}) has been determined by the relative magnitudes and signs of the different coefficients. For this the Ru(II)X$_2$ has been decomposed into three parts: Ru-1, X-1 and X-2, and the MO of the complete system has been obtained by allowing the orbitals of Ru-1 (4d, 5s, 5p), X-1 (ns and np) and X-2 (ns and np) to overlap. The possible overlaps between the various AOs of ruthenium (Ru-1) and halogens (X-2 and X-2) in each MO will be 88, as tabulated in Table-1.

Table-1. Overlaps between the various AOs of constituent's atom in each MO

NO	AO—AO	NO	AO—AO
1	(Ru-1)5s—ns(X-2)	45	(Ru-1)4dz^2—ns(X-3)
2	(Ru-1)5s—npx(X-2)	46	(Ru-1)4dz^2—npx(X-3)
3	(Ru-1)5s—npy(X-2)	47	(Ru-1)4dz^2—npy(X-3)
4	(Ru-1)5s—npz(X-2)	48	(Ru-1)4dz^2—npz(X-3)
5	(Ru-1)5s—ns(X-3)	49	(Ru-1)4dxy—ns (X-2)
6	(Ru-1)5s—npx(X-3)	50	(Ru-1) 4dxy—npx (X-2)
7	(Ru-1)5s—npy(X-3)	51	(Ru-1)4dxy—npy(X-2)
8	(Ru-1)5s—npz(X-3)	52	(Ru-1)4dxy—npz(X-2)
9	(Ru-1)5px—ns(X-2)	53	(Ru-1)4dxy—ns(X-3)
10	(Ru-1)5px—npx(X-2)	54	(Ru-1)4dxy—npx(X-3)
11	(Ru-1)5px—npy (X-2)	55	(Ru-1)4dxy—npy(X-3)
12	(Ru-1)5px—npz (X-2)	56	(Ru-1)4dxy—npz(X-3)
13	(Ru-1)5px—ns (X-3)	57	(Ru-1)4dxz—ns(X-2)
14	(Ru-1)5px—npx(X-3)	58	(Ru-1)4dxz—npx(X-2)
15	(Ru-1)5px—npy(X-3)	59	(Ru-1)4dxz—npy(X-2)
16	(Ru-1)5px—npz(X-3)	60	(Ru-1)4dxz—npz(X-2)
17	(Ru-1)5py—ns(X-2)	61	(Ru-1)4dxz—ns(X-3)
18	(Ru-1)5py—npx(X-2)	62	(Ru-1)4dxz—npx(X-3)
19	(Ru-1)5py—npy(X-2)	63	(Ru-1)4dxz—npy(X-3)
20	(Ru-1)5py—npz(X-2)	64	(Ru-1)4dxz—npz(X-3)
21	(Ru-1)5py—ns(X-3)	65	(Ru-1)4dyz—ns(X-2)
22	(Ru-1)5py—npx(X-3)	66	(Ru-1)4dyz—npx(X-2)
23	(Ru-1)5py—npy(X-3)	67	(Ru-1)4dyz—npy(X-2)
24	(Ru-1)5py—npz(X-3)	68	(Ru-1)4dyz—npz(X-2)
25	(Ru-1)5pz—ns(X-2)	69	(Ru-1)4dyz—ns(X-3)
26	(Ru-1)5pz—npx(X-2)	70	(Ru-1)4dyz—npx(X-3)
27	(Ru-1)5pz—npy(X-2)	71	(Ru-1)4dyz—npy(X-3)
28	(Ru-1)5pz—npz(X-2)	72	(Ru-1)4dyz—npz(X-3)
29	(Ru-1)5pz—ns(X-3)	73	(X-2)ns—ns(X-3)
30	(Ru-1)5pz—npx(X-3)	74	(X-2)ns—npx(X-3)
31	(Ru-1)5pz—npy (X-3)	75	(X-2)ns—npy(X-3)
32	(Ru-1)5pz—npz(X-3)	76	(X-2)ns—npz(X-3)
33	(Ru-1)4dx^2-y^2—ns(X-2)	77	(X-2)npx—ns(X-3)
34	(Ru-1)4dx^2-y^2—npx(X-2)	78	(X-2)npx—npx(X-3)
35	(Ru-1)4dx^2-y^2—npy(X-2)	79	(X-2)npx—npy(X-3)
36	(Ru-1)4dx^2-y^2—npz(X-2)	80	(X-2)npx—npz(X-3)
37	(Ru-1)4dx^2-y^2—ns(X-3)	81	(X-2)npy—ns(X-3)
38	(Ru-1)4dx^2-y^2—npx(X-3)	82	(X-2)npy—npx(X-3)
39	(Ru-1)4dx^2-y^2—npy(X-3)	83	(X-2)npy—npy(X-3)
40	(Ru-1)4dx^2-y^2—npz(X-3)	84	(X-2)npy—npz(X-3)
41	(Ru-1)4dz^2—ns(X-2)	85	(X-2)npz—ns(X-3)
42	(Ru-1)4dz^2—npx(X-2)	86	(X-2)npz—npx(X-3)
43	(Ru-1)4dz^2—npy(X-2)	87	(X-2)npz—npy(X-3)
44	(Ru-1)4dz^2—npz(X-2)	88	(X-2)npz—npz(X-3)

where, X-2 = Br (n=4) and X-3= Cl (n=3) for Ru(II)BrCl, X-2 = I (n=5) and X-3= Br (n=4) for Ru(II)IBr, and X-2 = I (n=5) and X-3= Cl (n=3) for Ru(II)ICl.

The number of electrons is taken as two for ϕ_1 to ϕ_{11} and zero for ϕ_{12} to ϕ_{17}. Finally, Eq.3 has been solved for eleven MOs with respect to each mixeddihalide. In order to get a precise description, the sum of

overlap population for the eleven MOs of Ru(II)BrCl, Ru(II)IBrand Ru(II)ICl has also been worked out and results are presented in tables 2-4, respectively.

Table-2. Nature of occupied molecular orbitals of Ru(II)BrCl

MO No.	$\Sigma n_{r-s,i}$	sign	Nature of MOs
ϕ_1	0.1604	(Positive)	Bonding
ϕ_2	0.1719	(Positive)	Bonding
ϕ_3	0.3051	(Positive)	Bonding
ϕ_4	0.1949	(Positive)	Bonding
ϕ_5	0.1949	(Positive)	Bonding
ϕ_6	0.0000	(zero)	Nonbonding
ϕ_7	0.0000	(zero)	Nonbonding
ϕ_8	0.2422	(Positive)	Bonding
ϕ_9	0.0504	(Positive)	Bonding
ϕ_{10}	0.0495	(Positive)	Bonding
ϕ_{11}	0.1626	(Positive)	Bonding

Table-3. Nature of occupied molecular orbitals of Ru(II)IBr

MO No.	$\Sigma n_{r-s,i}$	sign	Nature of MOs
ϕ_1	0.1358	(Positive)	Bonding
ϕ_2	0.2496	(Positive)	Bonding
ϕ_3	0.2372	(Positive)	Bonding
ϕ_4	0.1442	(Positive)	Bonding
ϕ_5	0.1471	(Positive)	Bonding
ϕ_6	0.0000	(zero)	Nonbonding
ϕ_7	0.0000	(zero)	Nonbonding
ϕ_8	0.1698	(Positive)	Bonding
ϕ_9	0.0064	(Positive)	Bonding
ϕ_{10}	0.0063	(Positive)	Bonding
ϕ_{11}	0.2292	(Positive)	Bonding

Table-4. Nature of occupied molecular orbitals of Ru(II)ICl

MO No.	$\Sigma n_{r-s,i}$	sign	Nature of MOs
ϕ_1	0.1585	(Positive)	Bonding
ϕ_2	0.2527	(Positive)	Bonding
ϕ_3	0.2523	(Positive)	Bonding
ϕ_4	0.1848	(Positive)	Bonding
ϕ_5	0.1848	(Positive)	Bonding
ϕ_6	0.0000	(zero)	Nonbonding
ϕ_7	0.0000	(zero)	Nonbonding
ϕ_8	0.1824	(Positive)	Bonding
ϕ_9	-0.0105	(Negative)	antibonding
ϕ_{10}	-0.0105	(Negative)	antibonding
ϕ_{11}	0.2270	(Positive)	Bonding

As can be seen from the Table-2 that among the eleven molecular orbital of Ru(II)BrCl, nine are bonding and two are nonbonding. The bonding molecular orbitals are ϕ_1–$\phi_5$and ϕ_8–ϕ_{11}. The nonbonding molecular orbital are ϕ_6 andϕ_7, which are purely two d atomic orbitals of ruthenium namely dxz and dz^2.Table-3 shows that among the eleven molecular orbital of Ru(II)IBr, nine are bonding and two are nonbonding. The bonding molecular orbitals are ϕ_1–$\phi_5$and ϕ_8–ϕ_{11}. The nonbonding molecular orbital are ϕ_6 andϕ_7, which are purely two d atomic orbitals of ruthenium namely dxz and dz^2.But, Table-4 shows that among the eleven molecular orbital of RuICl, seven are bonding, two are nonbonding and two are antibonding. The bonding

molecular orbitals are ϕ_1–ϕ_5, ϕ_8 andϕ_{11}. The nonbonding molecular orbital are ϕ_6 andϕ_7, which are purely two d atomic orbitals of ruthenium namely dxz and dz^2. Remaining two ϕ_9 andϕ_{10} are antibonding.A comparative study of tables, 2-4 reflected that in all cases the nonbonding electrons are present in 6th and 7th molecular orbitals. Further, similarity in positions of nonbonding molecular orbitals prompted us to examine the eigenvalues of Ru^{+2}ion and to compare them with the eigenvalues of their mixeddihalides. The energies of atomic orbitals of Ru^{+2}ion, and in its three halides are demonstrated in Scheme-4, which shows that all the d orbitals in Ru^{+2} ion are degenerate and their energy is –0.5476 eV.

Scheme 4. Splitting of d orbitals in Ruthenium(II) mixeddihalides

Energy (eV)	Ru^{2+}	Ru(II)BrCl	Ru(II)IBr	Ru(II)ICl
-0.4541			4dxy, 4dxz	
-0.4559				4dxy, 4dxz
-0.4621		4dxz, 4dxy		
-0.5476	4dx^2-y^2, 4dz^2, 4dxy, 4dyz, 4dxz	4dyz, 4dz^2	4dyz, 4dz^2	4dyz, 4dz^2
-0.5632			4dx^2-y^2	
-0.5787				4dx^2-y^2
-0.5841		4dx^2-y^2		

The energy of 4dyz, and 4dz^2 orbitals (–0.5476 eV) in all the halides are also same, which confirmed non-bonding MOs are these pure d-AOs of Ru-1. In case of chloride the energy of 4dx^2–y^{2}is -0.5934eV and in bromide and iodide, –0.5702eV and –0.5560eV respectively. The 4dxy, and 4dxz are degenerate in all the cases but their energies differ, being –4521eV in chloride, –0.4579eV in bromide and –0.4725eV in iodide.
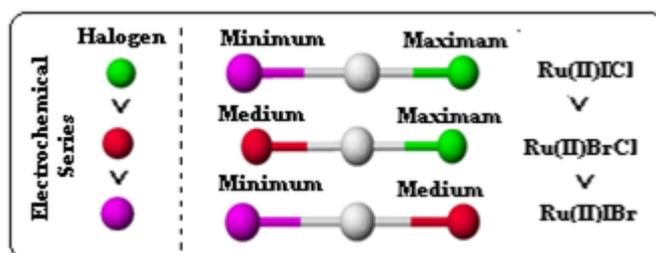
Scheme 5. Splitting effect of atoms in ruthenium mixeddihalides

The magnitude of splitting of metal d orbital has also been studied by calculating energy separation of nonbonding degenerate orbitals (4dyz, 4dz^2) and 4dx^2-y^2 or 4dxy, 4dxz. The highest value is in Ru(II)ICl and lowest in Ru(II)IBr. This is due to dominancy to one atom that has priority in electrochemical series, "I$^-$ < Br$^-$< Cl$^-$ < N$_3^-$ < F$^-$ < OH$^-$ < O$_2^-$ < H$_2$O < NCS$^-$ < py < NH$_3$ < en < bpy < phen < NO$_2^-$ < CH$_3^-$ < C$_6$H$_5^-$ < CN$^-$ < CO < H" to the other atom as shown by Scheme-5 [9].

IV. CONCLUSION

(i) The $\sum c_i$ clearly reflects maximum involvement is of 4d orbital (4dx^2-y^2> 4dxz > 4dxy). Next to this is 5s orbital. It is evident that major contribution is from 4d and 5s orbital. The 5p orbitals have negligible contribution, which is supported by their bond angles of sd-hybridization as proposed by Landis et al.

(ii) Further, $\sum c_i$ values follow the trend, Ru(II)ICl > Ru(II)IBr > Ru(II)ICl, which is due to dominancy of one atom that has priority in nephelauxetic series to the other atom. The dominancy of one atom to the otherdepends up on the difference in electronegativity of the halogens: ($\Delta\chi_{I-Cl}$= 0.5) > ($\Delta\chi_{I-Br}$ = 0.3) > ($\Delta\chi_{Cl-Br}$ =0.2).

(iii) The magnitude of splitting of ruthenium's d-orbitals follow the trendRu(II)ICl > Ru(II)BrCl > Ru(II)IBr, which is also due to dominancy of one atom that has priority in electrochemical series to the other atom.

(iv) Population analysis study shows in case of Ru(II)BrCl and Ru(II)IBr among the eleven molecular orbital, nine are bonding (BMO) and two are nonbonding (NBO). The BMOs are ϕ_1–$\phi_5$and ϕ_8–ϕ_{11}. The NBOs are ϕ_6 andϕ_7, which are purely two d atomic orbitals of ruthenium namely dxz and dz^2. While in Ru(II)ICl, among the eleven molecular orbital, seven are bonding (BMO), two are NBO and two are antibonding (ABMO). The BMOs are ϕ_1–ϕ_5, ϕ_8 andϕ_{11}. The NBOs are ϕ_6 andϕ_7, which are purely two d atomic orbitals of ruthenium namely dxz and dz^2. Remaining two ϕ_9 andϕ_{10} are antibonding.

(v) MOT reflected that all the MOs (ϕ_1–ϕ_{17}) have definite energy and definite shape due to (a) different contribution ($c_{ri}$and c_{si}) of many basis functions (χ_1–χ_{17}) (b) difference in energies ($\Delta\varepsilon$) of overlapping

AOs (c) difference in overlap integral (S_{r-s}) and (d) symmetry (phase) of overlapping AOs. And, thus provide clear cut electronic picture of the molecule, which more precisely can explain or help to explain the various properties of the complex compounds synthesized by these molecules, which can be a requisite for the synthesis of various ruthenium(II) complex compounds.

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