MOLECULAR MECHANICS BASED STUDY OF MOLECULAR ORBITALS OF COBALT (II) HALIDES

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ABSTRACT

The quantitative nature of contributions of atomic orbitals in in the formation of molecular orbitals with the help of LCAO approximations has been studied using eigenvector values. The contribution of electrons in each occupied molecular orbitals has been calculated by adopting the population analysis method of Mulliken. The overlap population analysis has been made to identify the bounding, non-bonding and antibonding nature of molecular orbital. The magnitude of splitting of d orbital as evaluated by eigenvalues and eigenvector values indicate the following order: $CoCl_2 < CoBr_2 < CoI_2$.
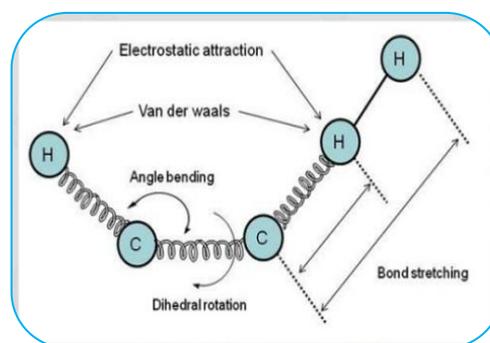
KEYWORDS: inhuman treatment , correctional systems , human rights.

INTRODUCTION

In the last decade, there has been a phenomenal advancement in theoretical inorganic chemistry, much faster computers are available and 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. Application of molecular mechanics to organomettalic and transition metal compounds is growing[12]. Molecular orbital parameters such as eigenvectors, oeverlap matrix and eigenvalues are well calculated with this method. In this paper we present the calculations of eigenvector, overlap matrix and population analysis of cobalt(II) halides, in order to study the extent of contribution of 3d, 4s and 4p orbital in the formation of molecular orbitals. Such a quantitative study will provide correct information about the involvement of 4p orbital of cobalt in bonding and will help to resolve the controversy raised by Landis[13-16] and other [17-21] workers.

EXPERIMENTAL

The Study Materials Of This Paper Are Halides of cobalt. 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

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function χ_r, which are used to express the MOs ϕ. as $\phi_1 = \Sigma c_{ri}\chi_r$ (c=coefficient of χr = number of atomic orbital, i=molecular orbital number). 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)[12, 22, 23]. Each molecular orbital ϕ_i, is expressed as $\phi_i = \Sigma c_{ri}\chi r$, where the χr's are the STO has basis functions. Here we use the STO-6G basis set (Which is contracted Gaussian) [24-27] for the SCF calculation.

Based on the above principle, the contributions of electrons in each occupied MO have been calculated with the help of eigenvector values. The overlap population analysis has also been made with the help of the values of eigenvector and overlap matrix for distinguishing the bonding, nonbonding and anti bonding nature.

RESULTS AND DISCUSSION

Cobalt (II) halides are tri atomic molecule, having the following optimized geometry[35-36] as obtained from molecular mechanics [37-40] method.

Bond length = 2.450 Å, bond angle = 117.37°   Bond Length = 2.300 Å, Bond Angle = 120°

Fig. 1a. Structure of $CoCl_2$ Fig. 1b. Structure of $CoBr_2$

Bond length = 2.488 Å, bond angle = 179.84°

Fig. 1c. Structure of CoI_2
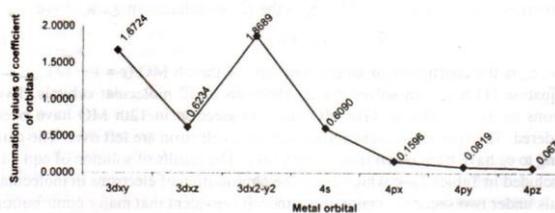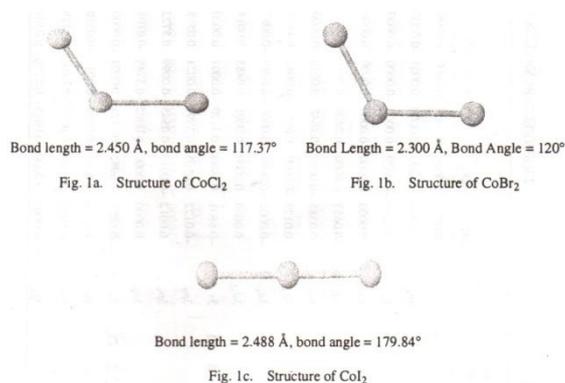
Fig. 2. Extent of involvement of metal orbital in the formation of MOs of $CoCl_2$
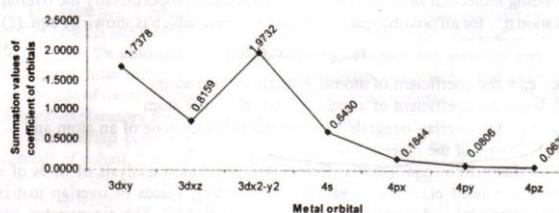
Fig. 3. Extent of involvement of metal orbital in the formation of MOs of $CoBr_2$
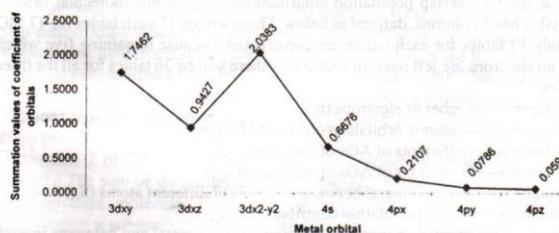
Fig. 4. Extent of involvement of metal orbital in the formation of MOs of CoI_2

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Population Analysis

the values of overlap populations decides the nature of MO in a covalent molecule. If the sum of this interatomic 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.

Similarly the sum of overlap population for the 12 MOs in all the halides has been worked out and the results are tabulated in Table-1.

TABLE-1
NATURE OF OCCUPIED MOs

MO No.	Sum of overlap-population contribution ($\Sigma nr\text{-}s, i$)		Nature of MOs
1	0.1238	(Positive)	Bonding
2	0.0461	(Positive)	Bonding
3	0.4744	(Positive)	Bonding
4	0.3976	(Positive)	Bonding
5	0.2197	(Positive)	Bonding
6	0.0588	(Positive)	Bonding
7	0.0590	(Positive)	Bonding
8	0.2095	(Positive)	Bonding
9	0.0000	(Zero)	Nonbonding
10	0.0000	(Zero)	Nonbonding
11	0.0079	(Positive)	Bonding
12	-0.1127	(Negative)	Antibonding

COBALT (II) BROMIDE

MO No.			
1	0.1292	(Positive)	Bonding
2	0.0563	(Positive)	Bonding
3	0.3553	(Positive)	Bonding
4	0.1579	(Positive)	Bonding
5	0.1814	(Positive)	Bonding
6	0.2362	(Positive)	Bonding
7	0.0000	(Zero)	Nonbonding
8	0.0000	(Zero)	Nonbonding
9	0.0423	(Positive)	Bonding
10	0.0418	(Positive)	Bonding
11	0.0340	(Positive)	Bonding
12	-0.0472	(Negative)	Antibonding

COBALT(II) IODIDE

MO No.			
1	0.181	(Positive)	Bonding
2	0.0751	(Positive)	Bonding
3	0.2857	(Positive)	Bonding
4	0.1243	(Positive)	Bonding
5	0.1243	(Positive)	Bonding
6	0.0000	(Zero)	Nonbonding
7	0.0000	(Zero)	Nonbonding
8	0.2409	(Positive)	Bonding
9	0.0331	(Positive)	Bonding
10	0.0332	(Positive)	Bonding
11	0.0577	(Positive)	Bonding
12	-0.0727	(Negative)	Antibonding

The population analysis as presented in Table-2 shows that the nonbonding electrons are present in 9th and 10th molecular orbitals in $CoCl_2$, 7th and 8th molecular orbitals in $CoBr_2$ and 6th and

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7th molecular orbitals in CoI_2. The difference in position of position of nonbonding molecular orbital prompted us to examine the eigenvalues of cobalt ion and to compare them with the eigenvalues of the halides. The eigenvalues of the molecular orbitals of the halides are included in Table-2. The nonbonding orbitals are degenerate in all the cases. The eigenvector indicates that these orbitals are $3d_{yz}$ and $3d_{z^2}$. The energies of these orbitals in cobalt ion and in its three halides are demonstrated in Table-3.

TABLE-2
EIGENVALUES OF ALL THE 17 MOs OF COBALT(II) HALIDES

MO No.	$CoCl_2$	$CoBr_2$	CoI_2
1	-0.9740	-0.8193	-0.6738
2	-0.9667	-0.8119	-0.6631
3	-0.5680	-0.5341	-0.5199
4	-0.5437	-0.5116	-0.5006
5	-0.5437	-0.5116	-0.5006
6	-0.5240	-0.4873	-0.4843
7	-0.5240	-0.4843	-0.4843
8	-0.5232	-0.4843	-0.4734
9	-0.4843	-0.4827	-0.4677
10	-0.4843	-0.4827	-0.4677
11	-0.4596	-0.4524	-0.4516
12	-0.4528	-0.4486	-0.4467
13	-0.4528	-0.4486	-0.4467
14	-0.1670	-0.1786	-0.1831
15	-0.1670	-0.1786	-0.1831
16	0.0767	-0.0620	-0.1075
17	0.3738	0.1780	0.0973

From Table-3, it is clear that all the d orbitals in ion are degenerate and their energy is -0.4843 eV. The energy of $3d_{yz}$ and $3d_{z^2}$ orbitals in all the halides is also -0.4843 eV. In case of chloride the energy of $3d_{x^2-y^2}$ is -0.4596 and in bromide and iodide -0.4524 and -0.4516 eV respectively. The $3d_{xy}$ and $3d_{xz}$ are degenerate in all the cases but their energies differ, being -0.4528 eV in chloride, -0.4486 eV in bromide and -0.4467 cV in iodide. If the magnitude of splitting, i.e., difference in energies of two nonbonding degenerate orbitals ($3d_{yz}$, $3d_{z^2}$) and $3d_{x^2-y^2}$ or $3d_{xy}$, $3d_{xz}$ is evaluated, the highest value is in iodide and lowest in chloride.

TABLE-3
SPLITTING OF d ORBITALS IN COBALT (II) HALIDES

Energy	Co^{++}	$CoCl_2$	$CoBr_2$	CoI_2
-0.4843	$3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$	$3d_{yz}$, $3d_{z^2}$	$3d_{yz}$, $3d_{z^2}$	$3d_{yz}$, $3d_{z^2}$
-0.4596	-	$3d_{x^2-y^2}$	-	-
-0.4528	-	$3d_{xy}$, $3d_{xz}$	-	-
-0.4524	-	-	$3d_{x^2-y^2}$	-
-0.4516	-	-	-	$3d_{x^2-y^2}$
-0.4486	-	-	$3d_{xy}$, $3d_{xz}$	-
-0.4467	-	-	-	$3d_{xy}$, $3d_{xz}$

The halogens center into bonding through their s and p orbitals. The two orbitals differ in energy significantly. It is worth noticing that energy difference in s and p orbitals of the chloride, bromide and iodide are not the same. In chloride it is -0.9665 (s) and -0.5218 (p), in bromide it is -0.8110 (s) and -0.4814 (p) and in iodide -0.6615(s) and 0.4667 (p). The difference between energy levels of s and p orbitals in chloride is -0.4447, in bromide -0.3296 and in iodide -0.1948. The order is

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chloride>bromide> iodide. In other words, the s and p orbitals in iodide are close as compared to s and p orbitals in bromide and chloride. The splitting of d orbitals in the three halides as discussed can be related with the energy levels of s and p orbitals of the halogens. The iodide in which the s and p orbitals are very close cause greater splitting in d orbitals or they have grater overlap with d orbitals of cobalt. It is perhaps on this account the splitting of d orbitals in iodide is more than chloride or bromide.

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

CONCLUSIONS
1. Eigenvector analysis shows that $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals of cobalt play a major role in bonding between cobalt and halogen, 4s orbital is next and 4p orbitals have a negligible role. This supports the Landis observation and concept of sd hybridization. The bond angles are also in the range prescribed for sd hybridization.
2. s and p orbitals of halogen are involved in bonding with cobalt. There is a difference in the energy levels of s and p orbitals in the three halides. The difference in chloride is 0.4447, in bromide 0.3296 and in iodide 0.1948. The closeness in the energy levels of s and p in iodide makes it more effective for overlap with orbitals of cobalt.
3. The overlap population analysis shows that nonbonding orbitals in chloride are 9th and 10th, in bromide 7th and 8th and in iodide 6th and 7th molecular orbitals. The energy of these orbitals in all the cases is-0.4843 eV. The degenerate d orbitals of Co^{2+} has also the same energy.
4. The magnitude of splitting of d orbitals as evaluated by eigen values and eigenvectors indicates the following order: $CoCl_2 < CoBr_2 < CoI_2$.
5. No molecular orbital is formed by two atomic orbitals only. All MOs have contribution from many atomic orbitals, the difference is only in extent of involvement.

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