CONSTRUCTION OF MOLECULAR ORBITAL SEQUENCE OF SILVER(II)–BIS–TRIPYRIDYL SYSTEM

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Abstract. Molecular orbital sequence of silver (II)-bistripyridyl system has been determined on the basis of symmetry characters of the molecule. Effort has been made to explain the symmetrical octahedral structure.

Only a few Ag(II) complexes have been reported so far. The stability of these complexes depends amongst other things on the type of ligand. Tripyridyl provides one such ligand which is known to have an extended π-bonding system.[1] Ag(II) bis-tripyridyl has been prepared and its IR spectrum repoted. The IR spectrum indicates all coordinating nitrogens to be equivalent,[1] and hence the molecule can be considered to have cubic symmetry and O_h point group. An attempt has been made to determine the molecular orbital sequence of the system based on group symmetry properties.

The σ-System of Metal Ion. The following reducible representation was worked out using position functions for σ-bonds.

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_r$
Γ_σ	6	0	0	2	2	0	0	0	4	2

The reducible representation can be broken down to irreducible representation using the relation.

$$n_i = \frac{1}{h} \Sigma_R \, \chi_r \,(R) \, \chi_i \,(R)$$

where n_i is number of times the i th irreducible representation appears in the reducible representation, h is the order of the group, $\chi_r\,(R)$ the character of matrix corresponding to operation R in reducible representation and $\chi_i\,(R)$ is the same in irreducible representation.

Using character table of O_h group Γ_σ was reduced to the following,

$$\Gamma_\sigma = a_{1g} + e_g + t_{1u}.$$

It can be shown that a_{1g} transforms like S orbits, e_g like d_{z^2} and $d_{x^2-y^2}$ and t_{1u} like p_x, p_y and p_z orbitals.[2]

Hybrid Orbitals on Metal Ion. Since $\Gamma_\sigma = a_{1g} + e_g + t_{1u}$ as shown earlier, the required orbitals resulting from the hybridization of these orbitals should be

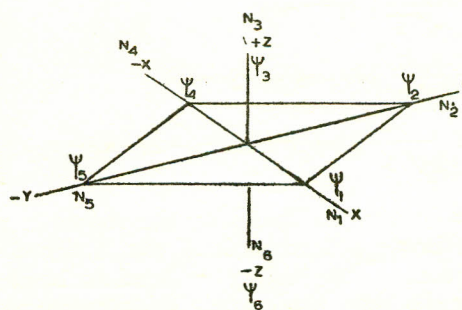$$\Psi_i = a_i \, S + b_i \, p_x + c_i \, p_y + d_i \, p_z + e_i \, d_{z^2} + f_i \, d_{x^2-y^2}$$

Fig. 1

Considering Fig. 1, it is evident that
Ψ_1 and Ψ_4 involves only S, p_x, d_{z^2}, $d_{x^2-y^2}$,
Ψ_2 and Ψ_5 involves only S, p_y, d_{z^2}, $d_{x^2-y^2}$,
Ψ_3 and Ψ_6 involves only S, P_z, and d_{z^2}, hence the following relations can be derived:

$$a_1 = a_2 = a_3 = a_4 = a_5 = a_6 = A$$
$$b_3 = b_6 = b_2 = b_5 = 0$$
$$c_3 = c_6 = c_1 = c_4 = 0$$
$$d_2 = d_5 = d_1 = d_4 = 0$$
$$\left.\begin{array}{l} b_1 = -b_4 \\ c_2 = -c_5 \\ d_3 = -d_6 \end{array}\right\} = B, \text{ as } p_x, p_y \text{ and } p_z \text{ are qeuivalent orbitals}$$
$$e_3 = e_6 = c$$
$$e_2 = e_5 = e_1 = e_4 = -1/2c$$
$$f_3 = f_6 = 0$$
$$f_2 = f_5 = -f_1 = -f_4 = D$$

The hybrid orbits using the coefficients derived above can be written as:

$$\Psi_1 = As + Bp_x - 1/2\, Cd_{z^2} + Dd_{x^2-y}{}^{-2}$$
$$\Psi_4 = As - Bp_x - 1/2\, Cd_{z^2} + Dd_{x^2-y}{}^{-2}$$
$$\Psi_2 = As + Bp_y - 1/2\, Cd_{z^2} - Dd_{x^2-y}{}^{-2}$$
$$\Psi_5 = As + Bp_y - 1/2\, Cd_{z^2} - Dd_{x^2-y}{}^{-2}$$
$$\Psi_3 = As + Bp_z + Cd_{z^2}$$
$$\Psi_6 = As - Bp_z + Cd_{z^2}$$

Since these orbitals must be orthogonal and normalized, the mixing coefficients can be calculated to be the following.[3]

$A = 1/\sqrt{6}, \quad B = 1/\sqrt{2}, \quad C = 1/\sqrt{3},$ and
$D = \frac{1}{2}$

The Ligand σ Orbital. Since we have

$\Gamma_\sigma = a1g + eg + t_1u$

suitable orbits from N-atoms of ligands that would transform like these irreducible representations should be constructed. If σ_i represents *ith* nitrogen atom we have the following set of orbitals.[4]

$$\varphi_I = \frac{1}{\sqrt{6}} (\sigma_2 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6) \quad a_1g$$

$$\varphi_2 = \frac{1}{\sqrt{2}} (\sigma_1\sigma - 4)$$

$$\varphi_3 = \frac{1}{\sqrt{2}} (\sigma_2 - \sigma_5) \quad \Bigg\} \quad .. \quad .. \quad .. \quad t_1u$$

$$\varphi_4 = \frac{1}{\sqrt{2}} (\sigma_3 - \sigma_6)$$

$$\varphi_5 = \frac{1}{\sqrt{2}} (\sigma_1 - \sigma_2 + \sigma_4 - \sigma_5)$$

$$\varphi_6 = \frac{1}{2\sqrt{3}} (2\sigma_3 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5) \quad \Bigg\} \quad eg$$

The π-System. To determine the reducible representation for π − systems each N was assigned three cartisian coordinates taking σ bond as band axis following the right hand rule. Each operation that changed coordinate system was considered to have character zero, the one that changed the sign of vector was assigned —1. and the other that left the vector unchanged was assigned +1.[5] Only X and Y vectors were considered for π bonds. The following reducible representation was obtained.

E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma\pi =$ 12	0	0	0	-4	0	0	0	0	0

This representation was broken down to the following irreducible representation using equation 1:

$$\Gamma\pi = t_1g + t_2g + t_1u + t_2u$$

Referring again to Oh character table it was found that Ag^{2+} ion has no t_1g and t_2u orbitals, while t_1u (px, py, pz) orbitals are engaged in σ −obonding which leaves only t_2g orbitals available for π − bonding with the central metal ion.[6]

The σ and π- orbitals available on the ligand are summarized in Table 1.

On the basis of the preceding discussion an approximate MO schematic was constructed as shown in Fig. 2. This schematic resembles Cu(II) MO as expected. A tetragonal distortion is predicted but since the ligand, tripyridyl, has an extended π — system and after Coordination would be expected to have small flexibility, an averaging effect of distortion can be expected which may be responsible for the apparent equivalence of the six metal–ligand bonds. The system requires detailed analysis of spectral transitions, calculations of group overlap integrals (Gij) and ligand –ligand interaction. This data would give a definite concl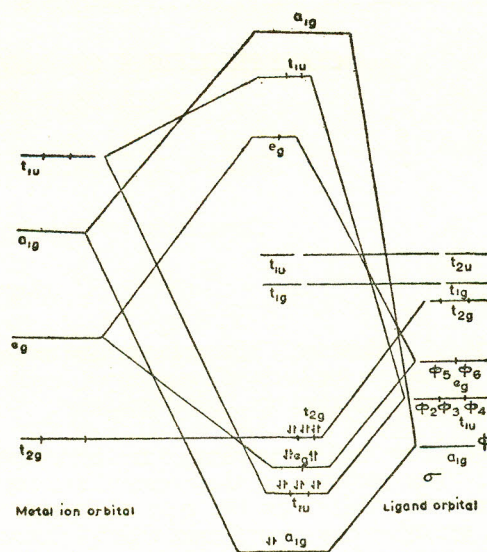usion regarding this system. However, the equivalence of all nitrogens shown by IR spectra is a strong evidence in support of the conclusion drawn above.

Fig. 2

TABLE 1

Oh	Ligand Group Orbitals
a_2g	$\frac{1}{\sqrt{6}} (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$
eg	$\frac{1}{2} (\sigma_1 - \sigma_2 + \sigma_4 - \sigma_5)$
	$\frac{1}{2\sqrt{3}} (2\sigma_3 + 2\sigma_6 + \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5)$
t_1g	$\frac{1}{2} (\pi_{y1} - \pi_{x3} + \pi_{x4} - \pi_{y6})$
	$\frac{1}{2} (\pi_{x2} - \pi_{y3} + \pi_{y5} - \pi_{y6})$
	$\frac{1}{2} (\pi_{x1} - \pi_{y2} + \pi_{y4} - \pi_{x5})$
t_1u	$\frac{1}{\sqrt{2}} (\sigma_1 - \sigma_4)$
	$\frac{1}{2} (\pi_{y2} + \pi_{x3} - \pi_{x5} - \pi_{y6})$
	$\frac{1}{\sqrt{2}} (\sigma_2 - \sigma_5)$
	$\frac{1}{2} (\pi_{x1} + \pi_{y3} - \pi_{y4} - \pi_{x6})$
	$\frac{1}{\sqrt{2}} (\sigma_3 - \sigma_6)$
	$\frac{1}{2} (\pi_{y1} + \pi_{x2} - \pi_{x4} - \pi_{y5})$
t_2g	$\frac{1}{2} (\pi_{y1} + \pi_{x3} + \pi_{x4} + \pi_{y6})$
	$\frac{1}{2} (\pi_{x2} + \pi_{y3} + \pi_{y5} + \pi_{x6})$
	$\frac{1}{2} (\pi_{x1} + \pi_{y2} + \pi_{y4} + \pi_{x5})$
t_2u	$\frac{1}{2} (\pi_{y2} - \pi_{x3} - \pi_{x5} + \pi_{x6})$
	$\frac{1}{2} (\pi_{x1} - \pi_{y3} - \pi_{y4} + \pi_{x6})$
	$\frac{1}{2} (\pi_{y1} - \pi_{x2} - \pi_{x4} + \pi_{y5})$

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