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## Paper-III

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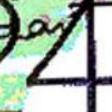
Inorganic chemistry

Basic Part - II

Valence bond theory [Continue]

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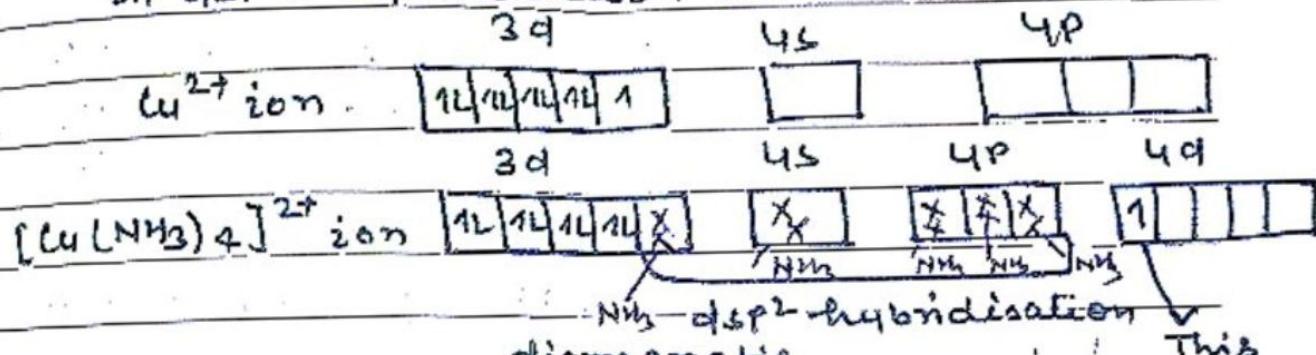
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Complex ion all the electrons are paired hence it is diamagnetic complexion. Some other similar examples are  $[PdCl_4]^{2-}$ ,  $[PtCl_4]^{2-}$ ,  $[Ni(NH_3)_6]^{2+}$ ,  $[Cu(NH_3)_6]^{2+}$  etc.

It is also interesting to note that the formation of  $[Cu(NH_3)_6]^{2+}$  ion, in this case one unpaired electron of 3d-orbitals is promoted to 4d-orbitals so that one empty 3d orbital may be involved in  $dsp^2$ -hybridisation which is shown below.



diamagnetic

This electron has

been promoted  
to higher energy  
level.

### (iii) Tetrahedral Complexes

Let us consider the formation

of  $[CuCl_4]^{2-}$  complex ion. The electronic configuration of Cu atom is  $1S^2, 2S^2, 2P^6, 3S^2, 3P^6, 3d^{10}, 4S^1$  and the  $Cu^{2+}$  ion has  $3d^{10}$  configuration. Now 4 Cl<sup>-</sup> ions approach

To  $Cu^{2+}$  ion, here all the 3d-orbitals are completely filled hence  $sp^3$ -hybridisation takes place to form a  $T$ -shaped  $Cu^{2+}$  ion. Since there is no unpaired electron

in the complex hence it is

S	M	T	W	T'	F	S	S	M	T	W	T'	F	S
1	2	3	4	5	6	7	8	9	10	11	12	13	14

15 16 17 18

19 20 21 22 23 24 25 26 27 28 29 30

diamagnetic in nature.

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Some Others

examples are  $[ZnCl_4]^{2-}$ ,

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$[Zn(NH_3)_4]^{2+}$ ,  $[MnCl_4]^{2-}$  etc.

3d

4s

4p

Cu atom

1L 1L 1L 1L 1L

1

1 1

3d

4s

4p

Cu<sup>+</sup> ion

1L 1L 1L 1L 1L

1

1 1

4s

4p

$[CuCl_4]^{3-}$  ion

1L 1L 1L 1L 1L

1

1 1 1 1

Q' C' C' C'

sp<sup>3</sup>- hybridisation  
in tetrahedral dimeric  
netic

Limitations of Valence bond theory

This theory is unable to explain no of the following facts.

1. It offers no Possibility of Predicting magnetic behavior except the no of Unpaired electrons in the complex.

2. Complex formation of certain metal ions is totally unsatisfactory because Cu<sup>2+</sup> forms complex ion in a d<sup>9</sup> species, d<sup>5</sup>p<sup>2</sup>- hybridisation is obtained by the promotion of one 3d-electrons to a higher level (4d-orbitals) Hence this should lead to ready oxidation of Cu<sup>2+</sup> to Cu<sup>3+</sup> a process which occurs rarely.

3. The theory does not explain why a Particular structure is preferred.

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e.g. of  $d^8$  ion

after maximum pairing in the excited state,  $d^8$ -ion may also form tetrahedral ( $sp^3$ -hybridisation) complexes which involves no excitation.

4. The theory offers no convincing explanation of causes of maximum pairing.

5. In this theory too much stress has been given of the metal ion while the nature of the ligands is not properly stressed.

6. This theory cannot explain reaction rate and maximum of the reactions.

7. It does not predict any distortion in symmetrical complexes whereas all the Cu(II) and Ti(III) complexes are distorted.

8. It does not explain thermodynamic properties of the complexes.

9. It does not attempt to explain the spectra of the complexes.

10. It cannot explain the temperature dependent paramagnetism of the complexes.