File-7: Applications of ESR Spectroscopy

- It decides about the **site of unpaired electron**(s)
- The number of line components decides the number and type of **nuclei** present in the **neighborhoods** of the odd electron.
- The relative intensities of the spectrum lines in as ESR spectrum confirm the **type of nuclei** which are responsible for the splitting pattern, summation of the intensities can be utilized to evaluate the total number of free electrons in the sample.
- From the ESR spectrum, the value of **g can be measured** by comparing the position of the line with that of a standard substance of known g value.
- If the electric field is not spherical, the ESR Spectrum is anisotropic., i.e. rotation of the sample shifts the ESR spectrum.

Bis salicylaldiminecopper(II) : CuL_2 ; L = Salicylaldimine = C_6H_4 CH = NH
{Bi dentate ligand with O & N as donors)
|
O^-

[I : Cu = 3/2 ; N = 1 ; H = ½]

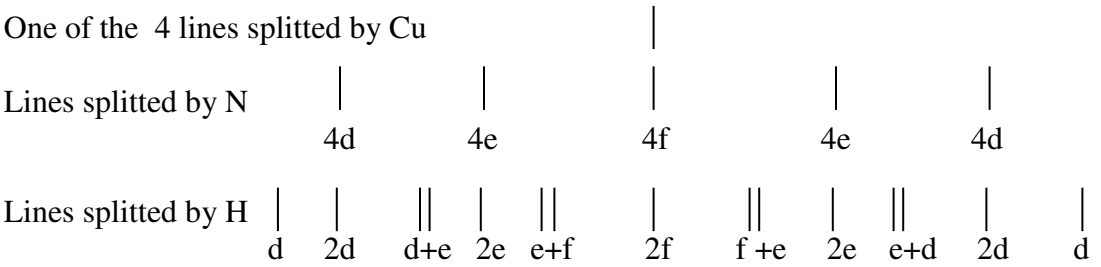
STRUCTCRE OF THE COMPLEX

(2x1x3/2+1)(2x2x1+1)(2x2x ½ +1) = 4 x 5 x 3 = 60 lines .

But, due to overlapping , we get 44 lines as 4 sets each consisting of 11 lines. The intensity of lines in each set is in the ratio 1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1

$J_{Cu} > J_N > J_H$

EMPERICAL FORMULATION OF THE LINES



Where , d = 1 , e = 2 , f = 3
So that the intensities of the lines are in the ratio
d : 2d : d+e : 2e : e+f : 2f : f +e : 2e : e+d : 2d : d
Which is 1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1

Deutration or methylation of protons in –CH = gives the same ESR spectrum.

But, deutration or methylation of protons in –NH = gives 20 lines only (4 sets of lines each set consisting of 5 lines)

These observations suggest that the odd electron in Cu^{2+} is delocalized on ligand and that too between N and Cu^{2+} which further supports metal-ligand covalent or back bonding or metal to ligand charge transfer (MLCT)

PRACTICE QUESTIONS IN ESR

1. Copper(II) acetate (Cu : I = 3/2) is a dimmer with copper atoms strongly attracting. The epr spectrum consists of seven lines with intensity ratio 1:2:3:4:3:2:1. Copper acetate consist of singlet ground state and triplet excited state .Explain the epr spectrum . What would be its signal intensity when it is cooled? Why?

2. Predict the epr spectrum of $(SO_3)_2NO_2^{-\cdot}$ anion radical.

3. The mono anionic radical ion , p-$^{-}$O-C_6H_4-$O^{-\cdot}$, can be prepared.

a) How many lines are expected in the ESR spectrum and what would be their relative intensities?

b) What evidence could be given and what experiments could be carried out to indicate electron delocalization onto the oxygen?

4. The ^{13}C hyperfine coupling in the methyl radical is 41 gauss and the proton hyperfine coupling is 23 gauss. Sketch the ESR spectrum and explain it for $^{13}CH_3\cdot$ radical.

5. Assuming that all hyperfine lines can be resolved , sketch the ESR spectrum of chloro benzene anion radical
6. How many lines would you expect in the ESR spectrum of SCl_3 (I : S = 0 ; Cl = 3/2)? Explain how this number arises and indicate the transitions with arrows. State their relative intensities.
7. Comment on the ESR spectrum of the following: $C_6H_5\cdot$, $C_6H_6^{+\cdot}$ and $C_6H_6^{-\cdot}$
8. Predict the ESR spectrum of naphthalene (i) radical (ii) anion radical and (iii) cation radical.
9. Calculate the number of ESR lines for $Cu(bpy)_3]^{2+}$ .I (Cu = 3/2 ; N= 1).
   Ans : (4 x 13) = 52 lines
10. ESR lines for $[Co(bpy)_3]^{3+}$; Ans : 0 lines
11. ESR lines for $[Co(H_2O)_3]^{2+}$; Ans : 8 lines
12. ESR lines for $[Mn(H_2O)_3]^{2+}$; I (Mn = 5/2) ; Ans : 6 lines
13. ESR lines for p-benzo quinine radical ; Ans : 5 lines due to 4H
14. ESR lines for Anthracine radical ; Ans :(3x 5 x5= 75) lines due to three types of hydrogen 2H, 4H , 4H.
15. ESR lines for $[(NH_3)_5\,CoO_2\,Co(NH_3)_5]^{5+}$
    O.No of both Co can be +3 and O_2 as O_2^- with one unpaired electron responsible for ESR.Ans:15 lines
16. ESR lines for $[(CH_3)_3C]_2\,N\text{-}O^-$ Ans: 3 lines due to 3N
17. ESR lines for biphenyl radical = 5x5x3=75 lines due to 4,4 ,1 = 9H
18. ESR lines for HO-C$^{\bullet}$H-COOH radical 3 lines due to –OH and –CH- protons.

REFERENCES.

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