Incase of $Cu_2(CH_3COO)_4 \cdot 2H_2O$, Cu(II) is d^9 system, electronic conf^n $t_{2g}^6 e_g^3$ having one ~~of~~ unpaired e^-. Thus the expected μ value is 1.73 BM

But observed magnetic moment < 1.73 BM

Because antiferromagnetism.

Factors which responsible for ~~a~~ antiferromagnetic behaviour, ~~these~~ these are–

i) ~~M~~ Direct M-M bond

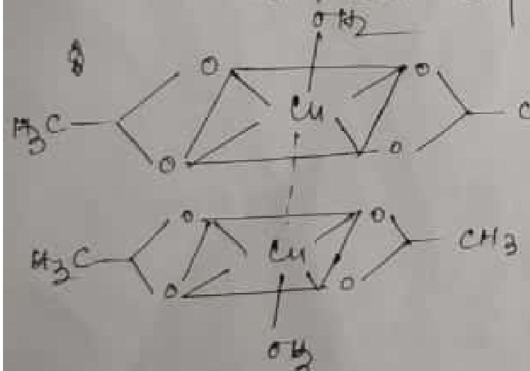
ii) Super exchange.

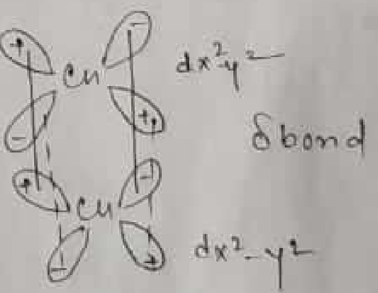
(1) Direct M-M bond :–

Cu^{2+} is d^9 system and the electronic arrangement becomes $d_{xy}^2\ d_{yz}^2\ d_{zx}^2\ d_{z^2}^2\ d_{x^2-y^2}^1$.

The unpaired e^- of $d_{x^2-y^2}$ orbital of ~~a~~ 2 Cu atom undergoes lateral overlap to form Cu-Cu δ bond. Thus the unpaired e^- of 2 Cu atoms ~~a~~ are being pair~~ed up~~.

But the δ bond is weak thats why we ~~get~~ ~~some~~ observe some magnetic moment which is small than expected.

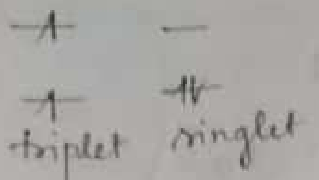




(ii) Super exchange :–

Super exchange mecha^m occurs throug the two Cu atom which are linked by acetate gr.

Both Cu atoms are singly ~~fille~~ occupied $d_{x^2-y^2}$ orbital & and the acetate ligand is doubly filled up. Thus the unpair e– of 2Cu atom becomes paired up with the ~~of~~ unpair e– of ligand. Thats why it shows such ~~ty~~ type μ value.



Due to the en b/w singlet & triplet is small. Thus the $Cu_2(CH_3COO)_4$ ~~[illegible]~~ possess both singlet & triplet state. When it ~~[illegible]~~ shows triplet state the, shows some magnetic moment which is less than expected.

- $[Cr_2(CH_3COO)_4]$

In such case, Cr^{+2} is d^4 system and the corresponding electronic arrange $\overset{1}{d_{xy}}\ \overset{1}{d_{yz}}\ \overset{1}{d_{zx}}\ \overset{1}{d_{z^2}}\ d_{x^2-y^2}$ orbitals contain unpaired e^- the d_{xy}, d_{yz}, d_{zx} & d_{z^2} of Cr^{+2} involve each. These 4 unpaired e^-s with other 4 e^-s of Cr^{+2} atom bond formation resulting a quadruple bond (1σ, 2π & 1δ).

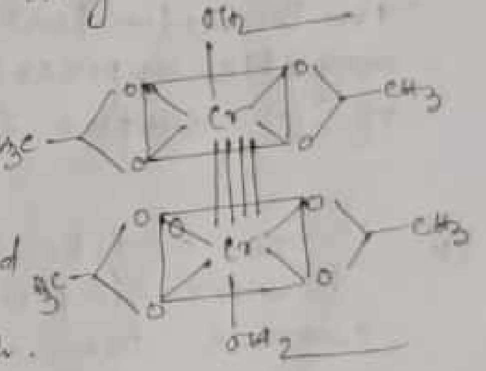
Thus all the 4 unpaire e^-s are paired up and the quadruple bond is more stronger than Cu-Cu bonds and thats why resulting magnetic moment is very low.

In case of $Cr_2(CH_3COO)_4$

(i) strong M-M bond

(ii) small distance of M-M bond

(iii) ~~e~~ extent of orbital overlap & J value is high.



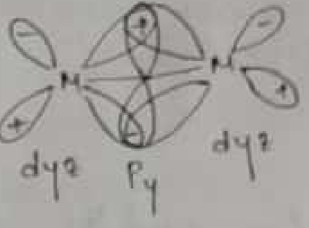
- $[(NH_3)_5\overset{III}{Cr}—O—Cr—(NH_3)_5]Br$ — ①

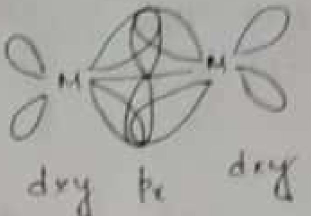
$[(NH_3)_5\overset{III}{Cr}—OH—Cr\ (NH_3)_5]Br$ — ②

The antiferromagnetic superexchange interaction is more efficient in case of oxo bridge complex than hydroxo bridge complex. This is explained by following ways—

① In complex ①, O is sp hybridised. Thus the s & p_z orbitals involve for bond formation but p_x & p_y orbitals are free which interacts with Cr 'd' orbitals & resulting two-type of π-type superexchange interaction.

$$\text{Cr—O—Cr} \rightarrow \left\{ \begin{array}{l} M(d_{xy}) \overset{\pi}{—} O(p_x) \overset{\pi}{—} M(d_{xy}) \\ M(d_{yz}) \overset{\pi}{—} O(p_y) — M(d_{yz})? \end{array} \right\}$$





But in case of (ii), O atom of —OH gr sp^2 hybridised, thus the s, p_z & p_y ~~ob~~ orbitals are involved for bond formation & only p_x orbital is free. This orbital interacts with metal 'd' orbital two give one ~~type~~ π-type superexchange interaction.

$$\text{Cr—OH—Cr} \rightarrow \left\{ M(d_{xy}) \overset{\pi}{—} O(p_x) \overset{\pi}{—} M(d_{xy}) \right\}$$

Thus the extent of π-type ~~super~~ antiferro-magnetic superexchange interaction in case of of ① complex than (ii).

(ii) The σ-type antiferromagnetic superexchange is more important for oxo ~~to~~ bridge complex than hydroxo bridge complex.

(iii) Complex ① has linear str. & complex (ii) has angular str. bending str. of Cr—OH—Cr linkge in hydroxido complex both σ & π type superexchange is less important.

If we go from CH_3COOH to CF_3COOH the μ values are ~~do~~ increases this is explained by antiferromagnetis behaviour of Cu atom.

When the no of ewg increases ~~or~~ in the acetate gr. the metal atoms becomes more +ve thats why the overlap b/w two $d_{x^2-y^2}$ orbitals of two Cu atom decreases & the distance b/w two $d_{x^2-y^2}$ orbitals increases and form weak δ bond. Since the antiferromagnetism property of Cu ~~atom~~ complex decreases & the resulting μ increases.

But in case CH_3COOH & $HCOOH$,

e^- donating ability of CH_3 gr is ~~grate~~ greater than 'H': Thats why the metal atom becoms more -ve in case of CH_3COOH ~~ting~~ ligand than $HCOOH$. When the metal atoms ~~is~~ ~~mo~~ have ~~more e~~ high e^- density overlap b/w $d_{x^2-y^2}$ orbital of 2 Cu atom increases and form strong δ bond. Since the antiferromagnetic property increases in case of CH_3COOH than $HCOOH$.

Thus the μ value of $HCOOH > CH_3COOH$.