

LIGHT ABSORPTION IN PARAMAGNETIC IONS IN STATE OF SOLUTION. PART I—CUPRIC IONS

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ABSTRACT. The light absorption from 3900 Å to 10,000 Å for eighteen cupric salts in aqueous solution have been studied with a Hilger "UVISPEK" spectrophotometer with an accuracy of 2 Å to 10 Å in different regions.

It is observed that Cu^{++} ions in aqueous solution have sharp absorption bands lying between 8110 Å and 6180 Å for different salts. The results are discussed in relation to the observed magnetic moments and g -values. From a study of the calculated covalency factors it is concluded that the mean magnetic moments do not change from salt to salt amongst the sulphates, chlorides and nitrates but are appreciably different for acetate, amines etc. In state of aqueous solution the salts are more ionic than in crystalline state if ΔE is the same. In ammosalts, acetate and propionate the covalency factor is made up of two factors arising from the σ and π orbital overlap.

1. INTRODUCTION

Extensive magnetic measurements on single crystals of cupric sulphate pentahydrate (Krishnan and Mookherji, 1936 & 1938) and other salts (Krishnan and Mookherji, 1938 ; Mookherji, 1945 , Bose, 1948 and Bose *et al.*, 1957) have revealed that magnetic behaviour of Cu^{++} ions in crystals may be explained in several details by assuming the Cu^{++} ions to be under the influence of a strong and asymmetric crystalline electric field arising out of an axially distorted octahedral cluster of water dipoles, surrounding the metal ion. The effect of such a field is to split the ground state of the ion into a Stark pattern. According to Bethe (1929, 1930) and others (Abragam & Pryce, 1951 and Owen, 1954) Stark splitting of the original ground state, ${}^2D_{5/2}$, of free Cu^{++} ion due to a crystalline electric field conforming to a potential

$$V = D(X^4 + Y^4 + Z^4) + A(X^2 + Y^2 - 2Z^2) + B(Z^4 + 6X^2Y^2) \quad (1)$$

is shown in figure 1, spin-orbit splitting being neglected. The first fourth degree terms in this expression represent a field of cubic symmetry the coefficient D of which is positive here (Gorter, 1932 and Van Vleck, 1932) and the remaining two terms represent the second and fourth degree components of the axial (tetragonal) field with symmetry about z -axis and both the coefficients are positive for the usual Cu^{++} salts (Bleaney, Bowers & Pryce, 1955; Abragam & Pryce, 1951 ; Bleaney, Bowers and Ingram, 1955 and Bose *et al.*, 1957).

A numerical estimate in $\text{Cu}(\text{KSO}_4)_2 \cdot 6\text{H}_2\text{O}$ by Polder (1942) using a model $\text{Cu}^{++}(\text{H}_2\text{O})_6$ gives the tetragonal splitting of the same order of magnitude as due to the cubic field. Experimental observations do not support this (Abragam and Pryce, 1951 and others).

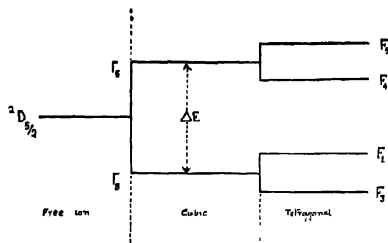


Fig. 1. Stark splitting of ground state of Cu^{++} ion.

According to these workers the cubic splitting may be taken as $\sim 10^4 \text{ cm}^{-1}$, and tetragonal splitting as $\sim 10^3 \text{ cm}^{-1}$. Hence the transitions between the levels so split will produce absorption spectra lying between ultraviolet and infra-red regions and as such will be capable of optical verification. Dresch and Trommer (1937) working on the selective absorption for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ in state of solution find that the absorption bands are roughly at $12,297 \text{ cm}^{-1}$ and $14,160 \text{ cm}^{-1}$ respectively.

In the state of solution of a given salt the lattice structure breaks down completely while the anisotropic ionic clusters retain their identities (Krishnan, 1939 and Chakravarty, 1942). But since they are oriented at random the medium will show no anisotropy of susceptibility. But optical absorption should reveal the fine structure in the Stark pattern arising from the anisotropic field splittings.

A systematic optical investigation of the consequences of the crystal field on the paramagnetic ions both in the crystalline state and in state of solution is under progress in this laboratory. The present communication deals with the absorption of light by a number of cupric salts in state of solution (aqueous) and are discussed in the light of the findings from magnetic measurements and paramagnetic absorption experiments.

2. EXPERIMENTAL

The selective absorption bands of paramagnetic salts of iron group of metals in state of solution show very broad absorption bands when photographed by a spectrograph; as such it is not possible to determine with any degree of accuracy, the position of the absorption maximum from an examination of the absorption

spectra of these salts with a spectrograph (Dreisch and Trommer, 1937). Consequently the measurements on light absorption were carried out by a Hilger's "UVISPEK" spectrophotometer.

The description of the instrument is available from the literature (H700.307/57887) supplied by the company. Interested readers may refer to it.

The image of the lamp was accurately focussed on the entrance slit. The wavelength drum was calibrated by a hydrogen discharge tube and a mercury discharge lamp. The absorption cells were cleansed thoroughly and their percentage of transmission checked. The wavelength drum was set to the desired wavelength and the absorption cell tray was set such that the reference medium was in the light beam. The test solutions were then brought one by one in the light beam and for each of them the percentage of transmission was directly noted from the scale for that wavelength. This was repeated for various wavelengths.

The absorption due to the solvent and the absorption cell was nullified by filling the absorption cell with the solvent and putting it in place of the reference medium. Chemicals used were of 'Merck's' analytical reagent quality.

The accuracy of the measurements in the region 10,000Å to 6500Å is approximately $10 \text{ Å} \pm 2\text{Å}$, from 6500Å to 5000Å is approximately $5\text{Å} \pm 1\text{Å}$ and from 5000Å to 3900Å is approximately $2\text{Å} \pm 1\text{Å}$. Measurements are centred round about 27°C but no observable change in the position of the absorption bands was noticed for small room temperature variations.

3. RESULTS

Results of the measurements are collected in Table I. The location of the absorption bands for various cupric salts in the state of solution are given both in wavelength and wavenumbers. In order to get prominent absorption peaks for the salts studied we had to use dilute solutions. Progressive dilution from that concentration at which prominent absorption peak is obtained does not change the position of the absorption peak.

The variation of absorption in different salt solutions are shown graphically in figures 2 to 19. No fine structure of the lines corresponding to tetragonal splitting could be observed.

4. DISCUSSION

(a) *Crystal field and energy levels*

According to the calculations of Polder (1942) the mean centres of the energy levels Γ_5 and Γ_3 (figure 1) are at $\frac{6}{21} D'$ and $-\frac{4}{21} D'$, where $D' = \frac{2}{5} e r^4 \cdot D$, D

TABLE I

S.No.	Salts	Concentration	Absorption (ΔE) at		$D' = 2.1\Delta E$	Remarks
			$\lambda \text{ \AA}$	Wave numbers cm^{-1}		
1.	CuSO_4	1.0	8060	12,405	26,055	Not sharp, lies between λ 8050 to λ 8075
2.	$\text{Cu}(\text{NH}_4\text{SO}_4)_2$	1.0	8050	12,420	26,085	Not sharp, lies between λ 8050 to λ 8063
3.	$\text{Cu}(\text{K}_2\text{SO}_4)_2$	1.0	8055	12,415	26,070	
4.	$\text{Cu}(\text{Rb}_2\text{SO}_4)_2$	1.5	8085	12,370	25,977	
5.	$\text{Cu}(\text{Tl}_2\text{SO}_4)_2$	1.0	8075	12,385	26,010	
6.	CuCl_2	1.0	8075	12,385	26,010	
7.	$2\text{NH}_4\text{Cl} \cdot \text{CuCl}_2$	1.0	8075	12,385	26,010	
8.	$2\text{KCl} \cdot \text{CuCl}_2$	1.0	8075	12,385	26,010	
9.	CuBr_2	1.1	8110	12,330	25,893	
10.	$\text{Cu}(\text{NO}_3)_2$	0.5	8060	12,405	26,055	
11.	$\text{Cu}_3\text{B}_{12}(\text{NO}_3)_{12}$	1.16	8075	12,385	26,010	
12.	$\text{Cu}(\text{CHOO})_2$	0.5	7775	12,860	27,005	
13.	$\text{Cu}(\text{CH}_3\text{COO})_2$	0.25	7675	13,030	27,360	
14.	$\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2$	0.4	7710	12,970	27,237	
15.	$[\text{Cu}(\text{NH}_3)_4](\text{SO}_4)$	$\left. \begin{matrix} .080 \\ 1 : 1 \end{matrix} \right\} \text{NH}_4\text{OH}$	6260	16,000	33,600	Band head changes with conc. of NH_4OH
16.	$[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$	$\left. \begin{matrix} .120 \\ 1 : 1 \end{matrix} \right\} \text{NH}_4\text{OH}$	6230	16,050	33,705	-do-
17.	$[\text{Cu}(\text{NH}_3)_4](\text{CH}_3\text{COO})_2$	$\left. \begin{matrix} .150 \\ 1 : 1 \end{matrix} \right\} \text{NH}_4\text{OH}$	6200	16,130	33,875	-do-
18.	$[\text{Cu}(\text{NH}_3)_4](\text{Cl})_2$	$\left. \begin{matrix} .150 \\ 1 : 1 \end{matrix} \right\} \text{NH}_4\text{OH}$	6180	16,180	33,980	-do-

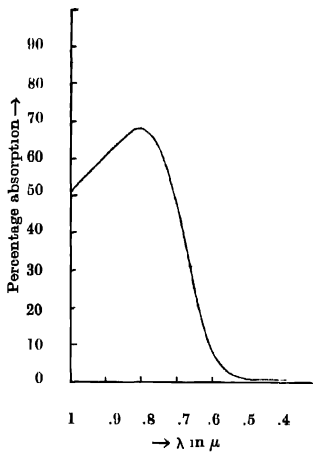


Fig. 2. Absorption curve of 1% CuSO_4 solution.

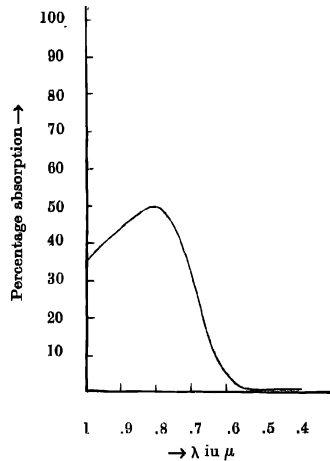


Fig. 3. Absorption curve of 1% $\text{Cu}(\text{NH}_4)_2\text{SO}_4$ solution.

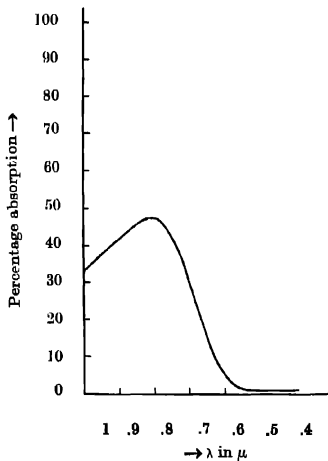


Fig. 4. Absorption curve of 1% $\text{Cu}(\text{K}_2\text{SO}_4)_2$ solution.

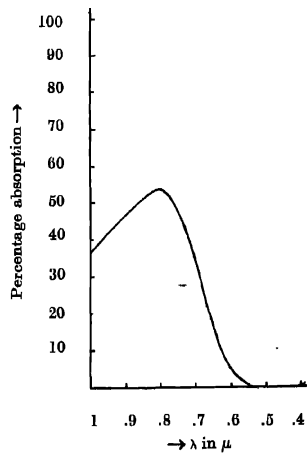


Fig. 5. Absorption curve of 1.5% $\text{Cu}(\text{Rb}_2\text{SO}_4)_2$ solution.

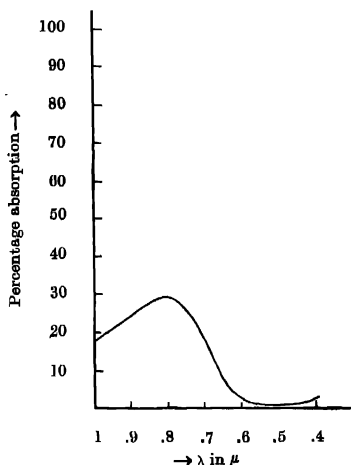


Fig. 6. Absorption curve of 1% $\text{Cu(Tl.SO}_4)_2$ solution.

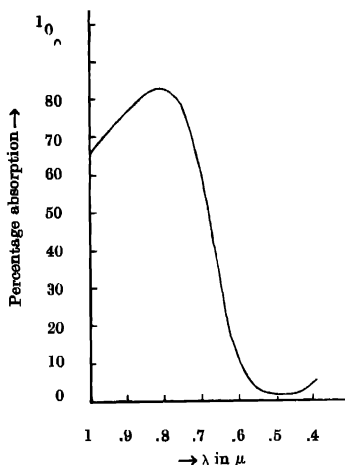


Fig. 7. Absorption curve of 1% CuCl_2 solution

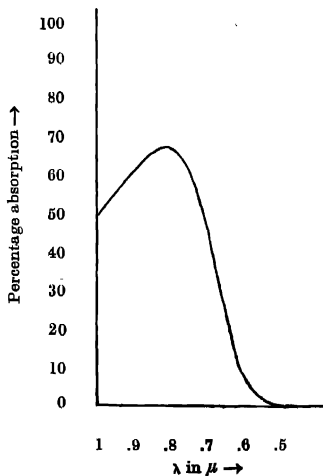


Fig. 8. Absorption curve of 1% $2\text{NH}_4\text{Cl.CuCl}_2$ solution.

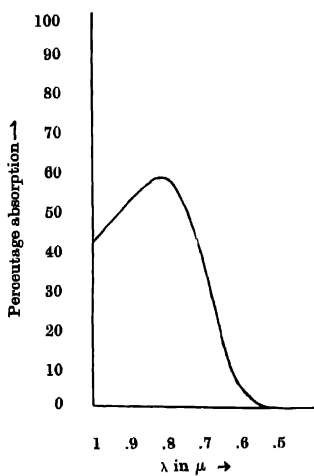


Fig. 9. Absorption curve of 1% 2KCl.CuCl_2 solution.

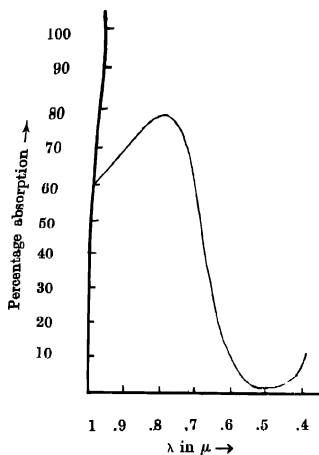


Fig. 10. Absorption curve of 1.1% CuBr_2 solution.

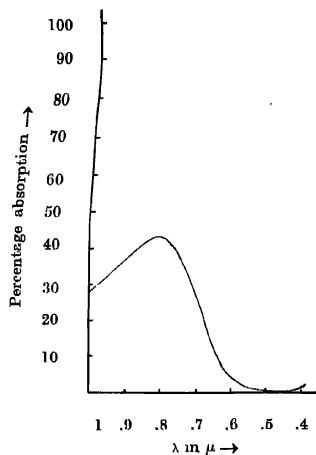


Fig. 11. Absorption curve of 0.5% $\text{Cu}(\text{NO}_3)_2$ solution.

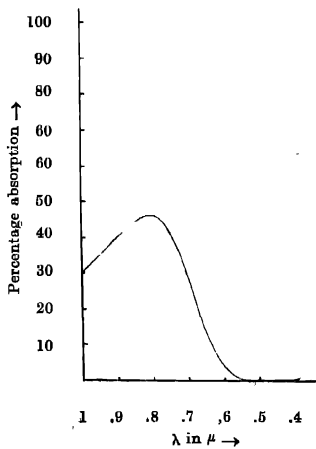


Fig. 12. Absorption curve of 1.16% $(\text{Cu}_3\text{Bi}_2(\text{NO}_3)_{12})$ solution.

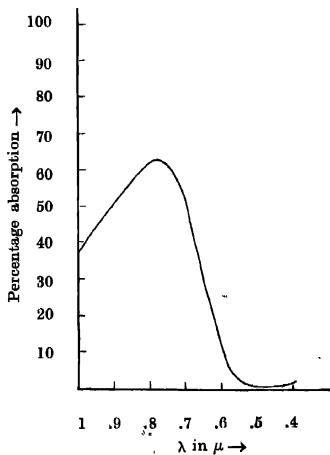


Fig. 13. Absorption curve of 0.5% $\text{Cu}(\text{CHOO})_2$ solution.

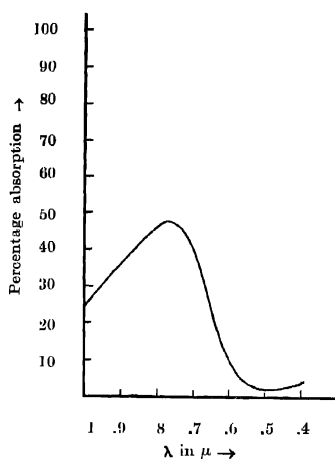


Fig. 14. Absorption curve of 0.25% $\text{Cu}(\text{CH}_3\text{COO})_2$ solution.

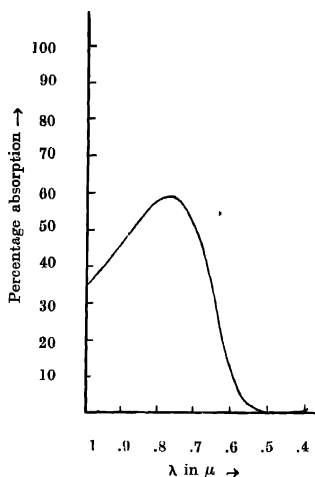


Fig. 15. Absorption curve of 0.4% $\text{Cu}(\text{CH}_3\text{COO})_2$ solution.

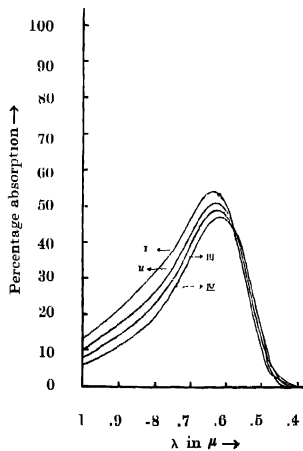


Fig. 16. Absorption curve of (all) .080% $\text{Cu}(\text{NH}_3)_4(\text{SO}_4)$ solution.

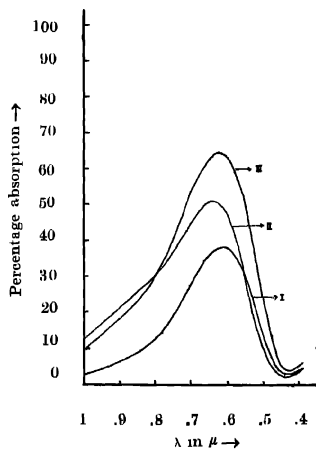


Fig. 17. Absorption curve of I, II, III .12%, .23% $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ solution.

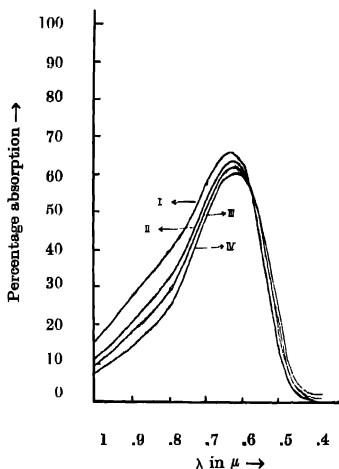


Fig. 18. Absorption curve of 0.15% $\text{Cu}(\text{NH}_4)_4(\text{CH}_3\text{COO})_2$ solution.

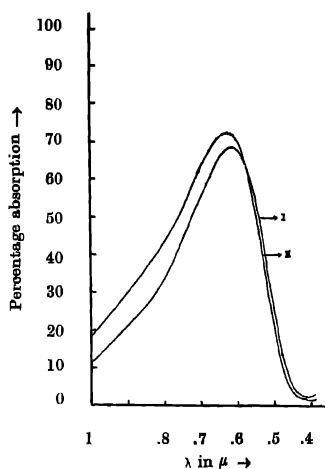


Fig. 19. Absorption curve of 0.15% $\text{Cu}(\text{NH}_3)_4(\text{Cl})_2$ solution.

being the cubic field coefficient (Eqn. 1) and r^4 is the average value of the fourth powers of the radii of $3d$ electrons. Thus ΔE , the cubic splitting is given by

$$\Delta E = \frac{10}{21} D' \quad \text{or} \quad D' = 2.1 \Delta E$$

Hence it will be interesting to calculate D' from the observed ΔE values which gives us an idea of the size of the octahedron of water molecules surrounding the Cu^{++} ion. This is given in Table I.

It will be seen from these values that the octahedral clusters about Cu^{++} ion are of nearly the same size in all the halides, $\text{Cu}(\text{TlSO}_4)_2$, $\text{Cu}(\text{RbSO}_4)_2$ and $\text{Cu}_3\text{Bi}_2(\text{NO}_3)_{12}$. Single sulphate, single nitrate and other double sulphates have also practically the same size of octahedron. This indicates further that in the solution state probably all the six members of the cluster are the same namely water molecules, though this was not the case in the solid state e.g. in the single sulphate and the halides. In copper formate, copper acetate and copper propionate solutions these octahedra are much smaller. Amino-salts have the smallest octahedra. Thus at least some of the coordination members in solution are very probably other than water molecules.

(b) Calculation of the covalency factor

Abraham and Pryce (1951) have calculated the "spectroscopic splitting factor" g in a tetragonal field for Cu^{++} ion in crystals. For directions parallel

and perpendicular to the tetragonal axis, neglecting square and product terms we have

$$\left. \begin{aligned} g_{\parallel} &= 2 - \frac{8\lambda \cdot f^2}{F_4 - F_3} \approx 2 - \frac{8\lambda}{\Delta E'} \\ \text{and} \\ g_{\perp} &= 2 - \frac{2\lambda \cdot f^2}{F_5 - F_3} \approx 2 - \frac{2\lambda}{\Delta E'} \end{aligned} \right\} \dots (2)$$

in which f^2 is the covalency factor arising from the partial overlap of the $3d$ orbitals with σ and π orbitals of the surrounding atoms (Owen 1954) assumed isotropic for the present; and $F_4 - F_3 \approx F_5 - F_3 = \Delta E = \Delta E' \cdot f^2$, is valid since the tetragonal separation in state of solution will be even less than $\sim 10^3 \text{ cm}^{-1}$ owing to the absence of the effect of the long range field in solution state (Bose & Mitra, 1952; Bose, Mitra and Datta, 1957).

Using experimentally determined g -values from paramagnetic resonance both for solids and liquids we have calculated $1/\Delta E'$, for the various salts using relation (3) taking $\lambda = -828 \text{ cm}^{-1}$ (Shenstone and Wilets, 1951).

$$g = \sqrt{\frac{g_{\parallel}^2 + 2g_{\perp}^2}{3}} \approx 2 \left(1 - \frac{2\lambda}{\Delta E'} \right) \dots (3)$$

These are given in Table III. It is observed that $1/\Delta E'$ values of solutions differ considerably from those of the solid values, indicating the effect of long range field as mentioned above.

Now following Polder (1942), Bleaney *et al* (1940) and Owen (1954) the principal moments along and normal to the tetragonal axis of the paramagnetic units calculated from the susceptibilities of the crystalline salts are

$$\left. \begin{aligned} \frac{\mu_{\parallel}^2}{3} &= \left(1 - \frac{4\lambda \cdot f^2}{F_4 - F_3} \right)^2 + \frac{8kT \cdot f^2}{F_4 - F_3} \\ \frac{\mu_{\perp}^2}{3} &= \left(1 - \frac{\lambda \cdot f^2}{F_5 - F_3} \right)^2 + \frac{2kT \cdot f^2}{F_5 - F_3} \end{aligned} \right\} \dots (4)$$

Taking as before

$$F_4 - F_3 \approx F_5 - F_3 = \Delta E = \Delta E' \cdot f^2$$

we have

$$\bar{\mu}^2 = (\bar{\mu}_{\parallel}^2 + 2\mu_{\perp}^2)/3 = \frac{3}{4}g^2 + \frac{12kT}{\Delta E'} = 3 \left[1 - \frac{4}{\Delta E'} (\lambda - kT) \right] \dots (5)$$

TABLE II

S.No.	Salts	g-values		μ - Values from g-Values		μ - Values from susceptibility	
		Crystal Solution		Crystal Solution		Crystal Solution	
1.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	2.208 ¹	2.184 ⁶	1.952	1.9265	1.923 ⁰	1.97 ⁰
2.	$\text{Cu}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	2.180 ²		1.922		1.938 ⁰	
3.	$\text{Cu}(\text{K}_2\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	2.184 ²		1.926		1.920 ⁰	
4.	$\text{Cu}(\text{Rb}_2\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	2.204 ²		1.947		1.930 ¹⁰	
5.	$\text{Cu}(\text{Tl}_2\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	2.177 ²		1.918		1.970 ¹⁰	
6.	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	2.1605	2.184 ⁸	1.902	1.9265	1.932 ¹¹	1.985 ⁰
7.	$\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl}$	2.160 ³		1.901		1.880 ¹⁰	1.967 ⁰
8.	$\text{CuCl}_2 \cdot 2\text{KCl}$	2.167 ³		1.908		1.850 ¹⁰	
9.	CuBr_2		2.175 ⁵		1.9175		2.000 ⁰
10.	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$		2.184 ⁸		1.9265	1.922 ¹²	1.956 ⁰
11.	$\text{Cu}_3\text{B}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	2.184 ⁴		1.962			
12.	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	2.150 ⁵					1.740
13.	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	2.164 ⁵		1.45		1.410 ¹⁰	1.488
14.	$\text{Cu}(\text{C}_2\text{H}_5\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$	2.184 ⁵					1.560
15.	$[\text{Cu}(\text{NH}_3)_4](\text{SO}_4)$	2.074 ⁷	2.100 ⁸	1.811	1.838	1.845 ¹³	
16.	$[\text{Cu}(\text{NH}_3)_4](\text{CH}_3)_2$		2.100 ⁸		1.838		
17.	$[\text{Cu}(\text{NH}_3)_4](\text{CH}_3\text{COO})_2$		2.100 ⁸		1.838		
18.	$[\text{Cu}(\text{NH}_3)_4](\text{Cl})_2$ ¶		2.100 ⁸		1.838		

1-Bauggley & Griffiths (1950), 2-Bleaney, Penrose and Plumpton (1949), 3-Abe, Ono, Hayashi, Shimada and Iwanaga (1954), 4-Trenam R. S. (1953), 5-Abe, (1953), 6-Mathur, S. C. (Unpublished, 7-Okamura and Dato (1954), 8-B.M. Kozyrev (1957), 9-Bose (1948), 10-Mookherji (1945), 11-Birch (1928), 12-Welo (1929), 13-Janes(1935).

TABLE III

S.No.	Salts	$1/\Delta E' \times 10^{-6}$				f^2			
		From g-values		From μ -values		From g-values		From μ -values	
		crystal solution	crystal solution	crystal solution	crystal solution	crystal solution	crystal solution	crystal solution	
1.	CuSO ₄ .5H ₂ O	62.8	55.6	54.7	68.9	.779	.689	.679	.855
2.	Cu(NH ₄ .SO ₄) ₂ .6H ₂ O	54.4		51.0		.676		.633	
3.	Cu(K.SO ₄) ₂ .6H ₂ O	55.6		53.5		.690		.664	
4.	Cu(Rb.SO ₄) ₂ .6H ₂ O	61.6		56.7		.702		.702	
5.	Cu(Tl.SO ₄) ₂ .6H ₂ O	53.5		68.2		.662		.844	
6.	CuCl ₂ .2H ₂ O	48.5	55.6	57.6	72.9	.600	.688	.713	.903
7.	CuCl ₂ .2NH ₄ Cl	48.3		42.0	67.45	.600		.520	.835
8.	CuCl ₂ .2KCl	50.4		33.6		.624		.416	
9.	CuBr ₂		52.84		94.85		.65		.990
10.	Cu(NO ₃) ₂ .3H ₂ O		55.6	54.3	64.2		.689	.674	.795
11.	Cu ₃ Bi ₂ (NO ₃) ₁₂ .24H ₂ O	66.0		54.3		.817		.672	
12.	Cu(CHOO) ₂ .4H ₂ O	45.3				.58		.028	.60
13.	Cu(CH ₃ COO) ₂ .H ₂ O	49.4		48.8	51.4	.644		.636	.67
14.	Cu(CH ₃ CH ₂ COO) ₂ .H ₂ O	55.6				.72			.68
15.	[Cu(NH ₃) ₄](SO ₄)	22.3	30.19	32.0		.357	.483	.512	
16.	[Cu(NH ₃) ₄](OH) ₂		30.19				.485		
17.	[Cu(NH ₃) ₄](CH ₃ COO) ₂		30.19				.489		
18.	[Cu(NH ₃) ₄](Cl) ₂		30.19				.487		

We have calculated the values of $\bar{\mu}$ from the resonance values of 'g' using the above equation and have given them for comparison with experimental susceptibility values of $\bar{\mu}$ for both solids and solutions in Table II.

The experimentally determined values do not agree with the calculated values. So we have calculated $1/\Delta E'$ from experimentally determined $\bar{\mu}$ -values of solids and solutions. There also the two values are different. Hence we presume that we can not utilize our optically observed value of ΔE from solutions to calculate f^2 for crystals. To get the values of f^2 for crystals we need optical data in crystal state. However, taking the $\bar{\mu}$ -values of solutions and using our optical data in state of solution, we have calculated f^2 for various cupric ions in state of solution which are given in Table III. It is seen that the single sulphate, the chloride, bromide and the nitrate are predominantly ionic; f^2 values tend to be ~ 0.9 in state of solution.

In the case of copper acetate according to Bleaney and Bowers (1952) pairs of Cu^{++} ions in the crystal are coupled together by exchange forces. Thus they will form a triplet state with parallel spin and a singlet state with anti-parallel spin. The triplet state will show a resonance spectrum similar to nickel salts with effective spin unity. Here again g is given by the expression (3). Using this expression and taking g for copper acetate from table II, we have calculated f^2 which is 0.644.

Bleaney and Bowers (1952) have deduced expressions for the principal susceptibilities for copper acetate from which $\bar{\mu}^2$ is given by

$$\mu^2 = 4 \left(1 - \frac{4\lambda \cdot f^2}{\Delta E} \right) \left[\frac{1}{1 + \frac{1}{4} e^{-J/RT}} \right] + \frac{12kT}{\Delta E} \cdot f^2 \quad \dots (6)$$

Taking $\bar{\mu}^2$ value for the crystal (Table II) using $J = -315 \text{ cm}^{-1}$ (Bleaney and Bowers, 1952) and our observed ΔE for solution we have calculated f^2 , which comes out as 0.636; now taking mean of these two values we have calculated J utilising $\bar{\mu}$ and ΔE values for solution which is found to be $\approx -270 \text{ cm}^{-1}$. If one calculates f^2 with $J = -315 \text{ cm}^{-1}$ as in crystal and $\bar{\mu}$ and ΔE for the solution f^2 comes out as 1.022 which is inadmissible. This anomaly may be attributed to the value of J which should be different in different states.

An examination of f^2 values in different states suggests that the most probable value of f^2 should be $\approx .67$, which gives the parameter $J = -275 \text{ cm}^{-1}$.

Anomalous resonance absorption spectra similar to copper acetate has been observed by Abe (1953) in case of copper propionate monohydrate. Our magnetic measurements on the moment of Cu^{++} ion in $\text{Cu}(\text{CH}_3\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$ salt in state of solution shows that $\bar{\mu} = 1.56$. These findings point to the fact that the

behaviour of Cu^{++} ions in the propionate will be similar to that of Cu^{++} ions in the acetate. Hence expression (6) is applicable in this case also.

Supplying experimental g -value and our observed ΔE for copper propionate in expression (3) we have calculated f^2 which comes out to be 0.72 (table II). Now substituting this values of f^2 and using $\bar{\mu}$ value for solution in the expression (6) we have calculated J the exchange integral which comes out to be -244 cm^{-1} . Since f^2 in solution is not the same as in solid state, hence this value of J will be slightly different in state of solution. Due to want of $\bar{\mu}$ value for the crystal it is not possible to suggest a most probable value for f^2 but a comparison of the solution $\bar{\mu}$ values of acetate and propionate suggests that f^2 should be almost like the acetate; hence taking f^2 as 0.68, J comes out $\approx -230 \text{ cm}^{-1}$.

The behaviour of Cu^{++} ion in formate from our observed ΔE value seems to be alike the acetate and propionate; but paramagnetic resonance spectrum as observed by Abe (1953) does not support this. The moment value as observed by us in state of solution goes to suggest that this is the limiting case between the Tutton salts with $\bar{\mu}$ values more than the spin-only value on one side and the acetate and propionate on the other with $\bar{\mu}$ values less than the spin-only value.

If Cu^{++} ions in formate behave like that in Tutton salts then f^2 from expression (5) comes out to be .028 which is inadmissible. This led us to presume that the behaviour of Cu^{++} ion in formate should be like those of the acetate and propionate.

On evaluating f^2 from the observed g -value in solid state and ΔE value from solution, it comes out as .58; but f^2 in state of solution should be different. A study of the f^2 values for propionate and acetate suggests that the probable value of $f^2 \approx .69$. This when substituted in (6) gives $J = -130 \text{ cm}^{-1}$, with $\bar{\mu} = 1.74$ as given in Table II. It is observed that the exchange integral in these three salts are in the right direction.

The acetate, propionate, formate and the amino-salts suggest that f^2 is really made up of two factors arising from the σ -orbital overlap and the other from π -orbital overlap eg., in the amino-salts f^2 may be, $f_\sigma^2 \sim .62$ and $f_\pi^2 \sim .85$ making $f^2 = f_\sigma^2 \cdot f_\pi^2 = .53$ as observed (very nearly so), while for the acetate, propionate and formate $f_\sigma^2 \sim .75$ and $f_\pi^2 \sim .9$ giving $f^2 = .68$ which is very near the observed values.

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