

## Studies on Absorption Spectra

### I. Results of Calculations on the Spectra and Configuration of Copper(II) Ions

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Various theories for absorption spectra are considered, particularly the theory of Hartmann and Ilse. In the present paper this theory is applied to the spectra of the ammine cupric ions in aqueous solution. The calculations performed show that the chemical and spectroscopical facts can be explained by assuming, with Orgel, a configuration with four planar and two more distant neighbours perpendicular to the plane. This explanation is based upon the crystal field theory of Bethe and van Vleck without taking into account electronic exchange between the cation and the ligands. The distances and dipole moments determined from the spectra in the red and near infrared show that the configuration deviates a few per cent from regular octahedral configuration. The spectra of the ammine complexes can be resolved into at least two bands in agreement with the theory. The theory can further predict the bands of the intermediate complex ions, and in the diammine spectrum allow the characterization of the *cis* band as well as a band belonging to the *trans*-diammine ion. A band in the near ultraviolet discovered by Winther and by Ley is shown to be caused by hydroxo-ammine complexes in small concentrations.

Many investigators have studied the absorption spectra of ions and complexes of the elements in the first transition group, and various theories have been proposed to explain the general appearance and origin of the different bands. After the picture offered by Bohr's atomic theory, it was generally assumed that the spectra were produced by electron transitions between different energy levels, but the difficulty was to decide which electrons were involved and between which levels they were jumping.

To account for the variety of colours observable for the same transition element with different ligands, Luther and Nikolopoulos<sup>1</sup> — even before the theory of Bohr — proposed that the spectra were due to "die atomare Struktur der Elektrizität, und die elektrische Natur der chemischen Bindung".

Ten years later Fajans <sup>2</sup> suggested that the colour was caused by the reciprocal influence of the electron system of the metal ion on the electrons of the ligand, paying much attention to the blue colour of the aquo cupric ion and the colourless anhydrous  $\text{CuSO}_4$ . These early suggestions were developed into two theories. Mead <sup>3</sup> was of the opinion that it was the ligands' co-ordinated electrons that were the causes of the bands, while Kato <sup>4</sup> assumed that the spectra in solution were the spectra of the naked ion deformed only by the environment. An explanation on similar lines was set forth by Bose and Mukherji <sup>5</sup>, and they proposed a formula for the mean frequencies of the absorption bands which did not correspond well with the experimental facts, however. Ideas from both schools were incorporated in Shibata's theory <sup>6</sup>, which was further developed by Tsuchida <sup>7</sup>. The spectra of  $[\text{Co}(\text{NH}_3)_{6-n}(\text{NO}_2)_n]^{(3-n)+}$ , for example, were divided into three bands, the first originating from the central ion, the second being due to the coordination electrons, and the third caused by anions in *trans*-position. If, in other compounds, there were more bands, they were denoted "special bands" and were considered to originate from different causes.

All these theories were rather *ad hoc* and indeed none of them could predict more than the experimental facts from which they were deduced. Tsuchida's theory was even proved wrong by the more elaborate work of Lindhard and Weigel <sup>8</sup>.

Such was the confusing state of affairs until Hartmann and Ilse <sup>9</sup> came forth with their theory for the spectrum of titanium(III) ions, utilizing ideas developed by Bethe <sup>10</sup> and in the school of van Vleck <sup>11</sup>. The hexaquo titanium(III) ion was assumed to have octahedral configuration. In that case Bethe <sup>10</sup> has proved that under the influence of a cubic crystal field, such as that provided by the six water dipoles, the energy level of the 3d electron will split up into two levels, transition of the 3d electron between which produces one band. The calculation makes use of the quantum-mechanical "perturbation theory", and as the ground system they considered the 3d electron moving in the field originating from the kernel, the field resulting from the water dipoles being treated as the perturbation. The calculations determine the frequency of the maximum of the band as a function of various parameters. Briefly:  $\nu_n = \mu \cdot f(R, Z)$ , where  $\mu$  is the point dipole moment of water, and  $f(R, Z)$  is a rather complicated function of  $R$ , the distance between the point dipole and the metal ion, and  $Z$ , the "effective" charge of the cation.

Putting  $Z$  for  $\text{Ti}^{+++} = 22 - 18 = 4$ ,  $\mu = 1.84$  Debye, *i. e.*, the permanent dipole moment of water, and  $R = 1.58$  Å, Hartmann and Ilse found that the maximum absorption of  $\text{Ti}(\text{H}_2\text{O})_6^{+++}$  was placed at  $570 \text{ m}\mu$ ; the experimental results <sup>9</sup> show it to be about  $490 \text{ m}\mu$ . Later Hartmann and Ilse <sup>12</sup> extended the theory to the more complicated system of 2 electrons, *viz.*  $\text{V}^{+++}$ , and also here the theory seems to be tolerably consistent with the experimental facts. But their interpretation of the theory predicts two bands for which the ratio of wavenumbers is 2.25, invariable with the chosen parameters, while the experimental ratio is about 1.4. Other features of the vanadium(III) spectra also deserve further investigation.

This application of the theory suggested to us that quantitative results might be obtained with  $\text{Cu}^{++}$ , an ion whose complexes and spectra are well

known. The Cu(II)-ion has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ , *i. e.* nine d-electrons outside the argon configuration. A relation originating from Pauli and proved for this special case by van Vleck<sup>13</sup> states that  $d^n \equiv d^{10-n}$ . This means that nine d-electrons give the same number of terms as one d-electron. The system is therefore treated analogously to the Ti(III)-ion. The complete calculations will be published elsewhere by C. J. Ballhausen, but the results are put to use and quoted here. Before we mention the results of the calculations, we shall first discuss the present state of the coordination chemistry of Cu(II).

#### COORDINATION CHEMISTRY OF COPPER(II) IONS

In the nomenclature of J. Bjerrum<sup>14</sup> the copper(II) ion has the characteristic coordination number 4. This is a way of expressing the fact that the solvated cupric ion, *e. g.* the aquo ion, when exchanging the water molecules consecutively with a ligand of not too different an interference volume<sup>15,16</sup>, takes up all of the first 4 ligands with about the same affinity and thereafter has only a slight affinity to take up more ligands.

Transition metals normally have the characteristic coordination number 6, but in some cases they have the characteristic coordination number 4, as *e. g.*, in the nickel(II)-cyanide and cobalt(II)-halide systems. If in such systems the metal ion has residual affinity to bind more than four ligand groups the maximum coordination number is usually 6, as demonstrated in the auric thiocyanate system, where the very stable  $Au(SCN)_4^-$  ion nearly statistically takes up two more ligands at relatively high thiocyanate concentrations<sup>17</sup>. For the cupric ammonia system Rosenblatt<sup>18</sup> and one of the authors<sup>19</sup> have shown independently that the rather stable tetrammine cupric ion is converted into a pentammine complex at higher ammonia concentrations. This was proved by spectrophotometric as well as by potentiometric methods<sup>20</sup>. Further, it was found that the pentammine spectrum estimated from mixed tetrammine-pentammine spectra in dilute ammonia solutions is but little different from the spectrum of the cupric ion in liquid ammonia<sup>20</sup>. For this reason it has hitherto not been possible to decide with certainty whether or not the cupric ion in solution is able to exceed the coordination number 5.

The conditions are different in the solid state where cupric salts besides tetrammines and pentammines — occasionally containing 2 and 1 water molecules, respectively — in many cases also form hexamminates<sup>14,p.98</sup>. Peyronel<sup>21</sup> found by X-ray analysis that  $Cu(NH_3)_6Br_2$  has face centered cubic structure and that the 6 ammonia molecules are octahedrally arranged around the copper ion, but this does not agree well with the fact that the crystals are mentioned to be optically anisotropic. The experimental evidence for an undistorted octahedral configuration is more certain for  $Ni(NH_3)_6Br_2$ , and for  $Zn(BrO_3)_2 \cdot 6 H_2O$ <sup>22</sup>, where it was shown directly from evidence of the precise positions of the ligands. It is also remarkable that according to West<sup>23</sup>,  $Cu(ClO_4)_2 \cdot 6 H_2O$  has monoclinic symmetry, while the series of analogous salt hydrates of zinc and the transition metals exhibits hexagonal symmetry. The hexacoordinated cupric compounds therefore cannot have a regular octahedral configuration, and it is very reasonable to assume, with Orgel<sup>24</sup>, a con-

figuration, with four planar and two more distant neighbours perpendicular to the plane. This configuration is also found in  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ <sup>25</sup>, where only four of the water molecules are co-ordinated to the copper ion, and two oxygen atoms from the sulphate ions are placed in *trans* positions to the plane formed by the copper ion and the 4 water molecules. A special configuration was recently<sup>26</sup> found for cupric acetate monohydrate in which the copper ion is coordinated to 5 oxygen atoms, and is directly linked to another copper atom at a distance of 2.64 Å.

It is interesting that the anhydrous pentammines and hexammines of the copper(II) halides form an isomorphous mixture<sup>27</sup> which has the same symmetry as the hexamine<sup>21</sup>, and therefore it cannot be excluded that in solution complex ions may exist with coordination number 5. The pentacyano nickel(II) ion was recently discussed as a possible case of this kind<sup>28</sup>.

Considering the fact that tetracoordinated cupric compounds according to X-ray analysis always seem to have a planar configuration, one of the authors<sup>14,p.108</sup> has postulated that the four groups corresponding to the characteristic coordination number are also co-planar in solution. The suggestion that the 5th ammonia molecule occupies an exceptional position is supported by the fact that the absorption band is displaced evenly toward blue by the uptake of the first four molecules of a monamine, or two molecules of a diamine, after which additional binding of one more amine molecule displaces the absorption maximum in the opposite direction.

In later publications J. Bjerrum *et al.*<sup>29,30</sup> and Klixbüll Jørgensen<sup>31</sup> gave more experimental evidence on the problem, and the results published here seems to permit a distinction to be made between the various possible configurations and to furnish a complete understanding of the stereochemistry of copper(II).

#### RESULTS OF CALCULATIONS OF SPECTRA OF COPPER(II)-COMPLEXES WITH DIPOLE MOLECULES

Four configurational possibilities are *a priori* considered in the calculations, *viz.* the square planar, the tetrahedral, the square pyramidal and the octahedral (*cf.* Fig. 1). In the models point dipoles are placed at the different sites of the configuration at a distance  $R$  from the centre of the metal ion, which is situated at the centre of the regular polyhedron; in the square-pyramidal configuration the copper ion is assumed to be placed at the midpoint of the square.

As already mentioned, the quantum-mechanical calculations lead to expressions for the wavenumber of the maximum of the bands. When the  $R$ -values are all equal, these functions are of the form:

$$\Delta E_n = hc\nu_n = \mu \left(\frac{Z}{3}\right)^2 \left\{ K_M \left(\frac{3}{ZR}\right)^M - \sum_N P_N \cdot e^{-\frac{2ZR}{3}} \right\} \quad (1)$$

where  $K_M$  is a constant and  $P_N$  polynomials of integral degrees of  $\left(\frac{3}{ZR}\right)$ . Of the parameters, the effective charge  $Z$  on the cupric ion is taken as 7.85 a.u., after Slater's screening theory for hydrogen-like wave functions<sup>32</sup>. The distance  $R$  is usually known from X-ray analyzed structures of the solid com-

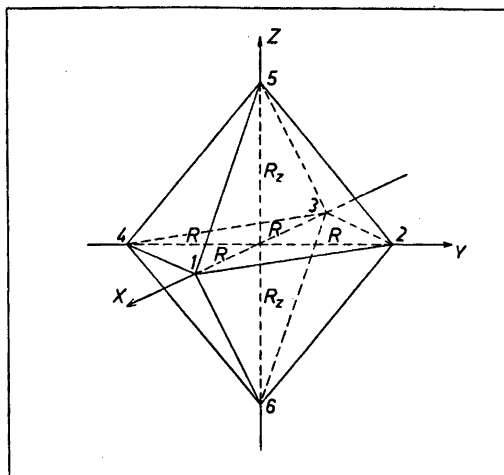


Fig. 1. Model of various types of complexes. The positions labelled 1-4 represent the the square, 1-5 the square pyramid, and 1-6 the octahedron (or tetragonal bipyramid).

plex salts, and it is reasonable to assume that the same values for  $R$  can be used for the distances of the metal ions to their nearest neighbours in solution. In the crystalline salt hydrates of the divalent metal ions in the first transition group  $R$ -values are usually found to be very nearly  $2 \text{ \AA}$ <sup>33</sup>. Thus Beevers and Lipson<sup>25</sup> determined the distance  $\text{Cu-H}_2\text{O}$  in the plane to be  $1.96 \text{ \AA}$  in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . By studying the influence of the refractive index on the light absorption Schuyer<sup>34</sup> estimates the same distance in aqueous solution to be  $2.01 \text{ \AA}$ . In the analogous ammoniates the distances are perhaps a little higher<sup>21,23</sup>, but are not known with the same accuracy<sup>33</sup>, and in the calculations reported here distances  $\text{Cu-H}_2\text{O}$  and  $\text{Cu-NH}_3$  are put equal. The least known of the parameters is  $\mu$ , the effective dipole moment of the ligand. This quantity is considered to be the sum of the permanent dipole moment and the induced dipole moment. The permanent dipole moment for water has the value  $1.84 \text{ D.}$ , and for ammonia the value  $1.44 \text{ D.}$ ; the induced dipole moment, on the other hand, cannot be estimated from the polarizability of the ligand because of the very strong electric fields within the complex.

Under the influence of the outer fields the five-fold degenerate  $^2\text{D}$ -state of the cupric ion splits up into a number of energy levels, the actual number depending on the symmetry of the field. Of the four models considered the regular tetrahedron and octahedron give two energy levels, while the less symmetrical square and square pyramid give 4 levels. The bands arise because of transitions between the ground level and the higher ones. Thus the regular tetrahedral and octahedral configurations both give one band ( $\gamma_5^6\gamma_3^3 \approx \gamma_5^5\gamma_3^4$ , cf. Santen and Wieringen<sup>35</sup>), whilst the two other configurations should theoretically give 3 bands.

Table 1. Results of calculations of models of copper (II)-ion dipole complexes with equal distance to all ligands.

The wavelength of the band of highest frequency  $\lambda_1$  (in  $m\mu$ ) is given as function of the parameters:  $R$  in Å,  $\mu$  in Debye.

a. The square planar case							
$R$	$\mu =$	1.84	2.00	3.00	4.00	5.00	6.00
1.72		810	740	500	370	300	250
1.84		1 100	1 000	670	500	400	340
2.00		1 620	1 490	990	740	590	500
2.20		2 380	2 190	1 450	1 090	880	730
2.40		3 450	3 180	2 110	1 590	1 270	1 060
b. The tetrahedral case							
$R$	$\mu =$	1.84	2.00	3.00	4.00	5.00	6.00
1.72		3 200	2 940	1 960	1 470	1 180	980
1.84		4 590	4 220	2 810	2 110	1 690	1 410
2.00		7 180	6 600	4 390	3 300	2 640	2 200
2.20		13 500	12 400	8 270	6 220	4 960	4 150
2.40		22 700	20 900	13 900	10 400	8 320	6 960
c. The square pyramidal case							
$R$	$\mu =$	1.84	2.00	3.00	4.00	5.00	6.00
1.72		1 040	960	640	480	380	320
1.84		1 440	1 320	880	660	530	440
2.00		2 200	2 020	1 350	1 010	810	670
2.20		3 460	3 190	2 120	1 590	1 280	1 060
2.40		5 320	4 890	3 260	2 450	1 960	1 630
d. The octahedral case							
$R$	$\mu =$	1.84	2.00	3.00	4.00	5.00	6.00
1.72		1 430	1 320	880	660	530	440
1.84		2 060	1 900	1 270	950	760	630
2.00		3 390	3 110	2 070	1 550	1 250	1 040
2.20		5 750	5 290	3 520	2 640	2 120	1 760
2.40		9 860	9 080	6 050	4 540	3 620	3 030

The wavelength  $\lambda_1$  of the maximum of the band of highest frequency in the various cases, calculated by insertion in the functions (1), are given in Table 1. The maximum for the aquo cupric ion is situated at 790  $m\mu$ , the maximum for the cupric ion in liquid ammonia at 640  $m\mu$ , and that for the tetrammine cupric ion at 590  $m\mu$  (see Figs. 2 and 3). It is readily seen from the table that these maxima are impossible to explain assuming tetrahedral, and difficult to explain assuming regular octahedral configuration, since  $R$  cannot be very different from 2 Å and there must also be a limit to the size of  $\mu$ . In the two other configurations considered, the ratio of the wavenumbers of the maxima of the possible bands has definite values for a given value of  $R$

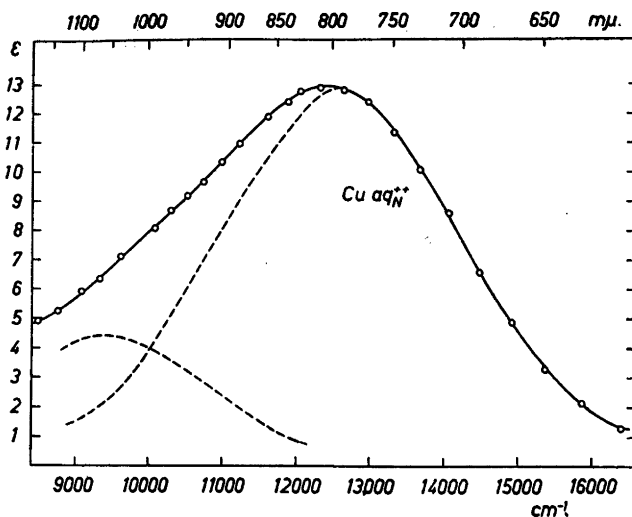


Fig. 2. Absorption spectrum of an aqueous cupric nitrate at 25° C ( $C_{\text{Cu}(\text{NO}_3)_2} = 0.01 \text{ M}$ ,  $C_{\text{HNO}_3} = 0.02 \text{ M}$ ,  $C_{\text{NH}_4\text{NO}_3} = 2.00 \text{ M}$ ), measured with a Beckman DU spectrophotometer. Analysis by the principle of symmetrical partial bands. o—o Experimental points, — — — analyzed band.

according to (1). The values of  $\lambda_2/\lambda_1$  corresponding to the square planar and square pyramidal configurations for selected values of  $R$  are given in Table 2. Table 2 also gives the dipole moment  $\mu$  for hypothetical complex ions of the configurations mentioned, and the wavelengths of the two possible bands of

Table 2. Wavelength ratios, dipole moments and wavelengths of possible bands (in  $m\mu$ ) according to the theory for square planar, square pyramidal and regular octahedral models of  $\text{Cu}(\text{II})$ -ion dipole complexes. ( $R$  in  $\text{Å}$ ,  $\mu$  in Debye).

Formula	Configuration	$R$	$\nu_1/\nu_2 = \lambda_2/\lambda_1$	$\mu$	$\lambda_1$	$\lambda_2$	$\lambda_3$
$\text{Cu aq}_4^{++}$	square planar	1.8	1.87	2.30	(790)	1 480	$> 10^4$
»	»	2.0	2.07	3.75	»	1 635	»
»	»	2.2	2.39	5.50	»	1 890	»
$\text{Cu am}_4^{++}$	»	1.8	1.87	3.09	(590)	1 110	»
»	»	2.0	2.07	5.04	»	1 220	»
»	»	2.2	2.39	7.40	»	1 410	»
$\text{Cu aq}_5^{++}$	square pyramid	1.8	1.67	3.00	(790)	1 320	1 380
»	»	2.0	1.66	5.06	»	1 310	1 330
»	»	2.2	1.64	8.11	»	1 300	1 290
$\text{Cu am}_5^{++}$	»	1.8	1.67	3.72	(640)	1 070	1 100
»	»	2.0	1.66	6.27	»	1 060	1 070
»	»	2.2	1.64	10.04	»	1 050	1 040
$\text{Cu aq}_6^{++}$	octahedral	1.8	1.00	4.35	(790)	—	—
»	»	2.0	»	7.83	»	—	—
»	»	2.2	»	13.6	»	—	—
$\text{Cu am}_6^{++}$	»	1.8	»	5.39	(640)	—	—
»	»	2.0	»	9.70	»	—	—
»	»	2.2	»	16.85	»	—	—

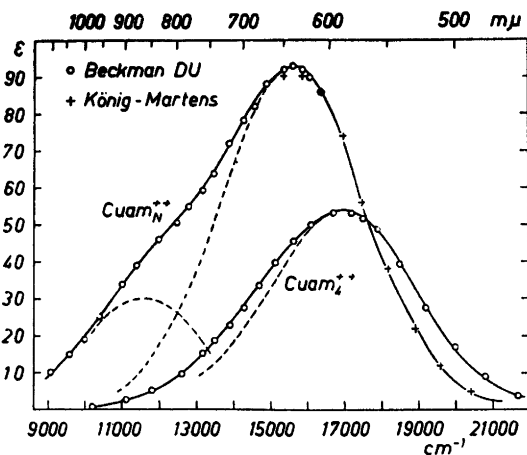


Fig. 3. Analysis of the absorption curve of cupric nitrate in liquid ammonia<sup>20</sup> ( $\text{Cu am}_N^{++}$ ), and of tetrammine cupric ion ( $\text{Cu am}_4^{++}$ ) in water. o-o New measurements, --- analyzed band.

lower frequency corresponding to the measured values of  $\lambda_1$ . For comparison the values of  $\mu$  corresponding to  $\lambda_1$  in the cases of octahedrally built aquo and ammine complexes are also given.

Cupric ions in aqueous solution apparently have only one band, but a closer examination of the absorption curve given in Fig. 2 shows that this spectrum is a superposition of more than one band. According to one of us (Klìxbüll Jørgensen, to be published) there is a great deal of experimental evidence that absorption curves (the extinction coefficient as function of the wavenumber) follow a simple Gaussian error curve, and consequently are symmetrical around their maximum value if the band is arising from a single transition. If this principle is used on the spectrum of the aquo cupric ion the experimentally determined absorption curve can be resolved into at least two symmetrical absorption curves with maxima at 790 and 1060  $m\mu$ , corresponding to the ratio of wavelengths  $\lambda_2/\lambda_1 = 1.34$ .

Fig. 3 shows the curve for cupric nitrate in liquid ammonia ( $\text{Cu am}_N^{++}$ ). The second maximum is here directly noticeable, and it is especially noteworthy that the ratio of wavelengths is very nearly the same as that found for cupric ions in aqueous solution. Analyzed as above we find  $\lambda_1 = 640$ ,  $\lambda_2 = 855$   $m\mu$ , giving  $\lambda_2/\lambda_1 = 1.33$ .

The experimentally determined wavelength ratio gives direct information about the configuration of the complex ions. This is easily seen in the following way: in going from the square to the square pyramidal configuration by gradually moving a point dipole along the Z-axis from infinity to  $R_5 = R$  (see Fig. 1), the ratio of wavelengths  $\lambda_2/\lambda_1$ , according to the theory, should decrease steadily from  $\sim 2$  to  $\sim 1.6$  (see Table 2). Now if the saturated aquo and ammine cupric ions have square pyramidal configurations with  $R_5 > R$ , one should expect  $\lambda_2/\lambda_1 > 1.6$ . The opposite is found, and as far as we



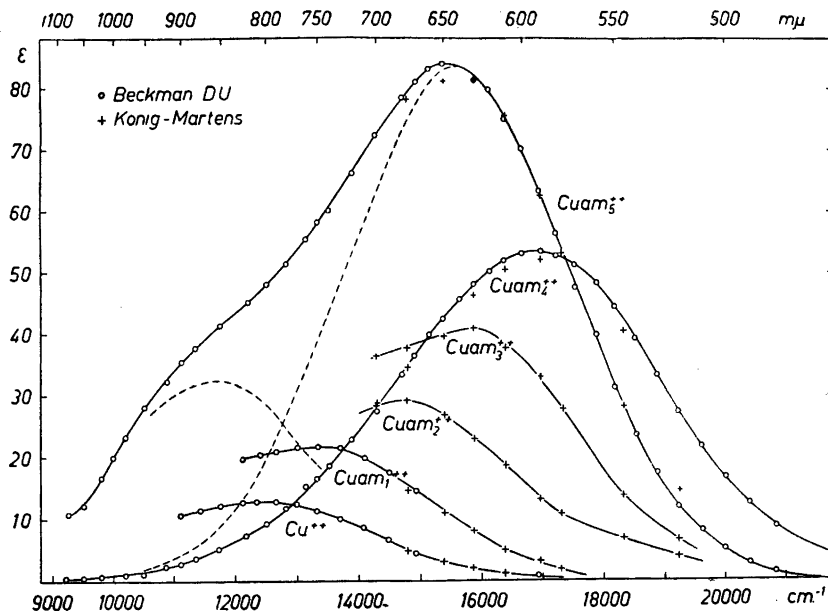


Fig. 4. Absorption spectra of copper (II)-ammonia complexes in 2 M ammonium nitrate at 20–25° C. Curves for  $\text{Cu}^{++}$  (see Fig. 2), and for the intermediate ammine cupric ions<sup>19</sup>. The curve for  $\text{Cu am}_1^{++}$  in the infrared as well as the curves for  $\text{Cu am}_4^{++}$  and  $\text{Cu am}_5^{++}$  are computed from new measurements with a Beckman DU spectrophotometer. Analysis by the principle of symmetrical partial bands (— analyzed band for  $\text{Cu am}_5$ ).

can see the only way to explain the observed ratio  $\sim 1.3$  in water as well as in liquid ammonia is to assume, with Orgel<sup>24</sup>, a tetragonal bipyramidal configuration for the copper(II) ions.

According to the theory, point dipoles placed along the Z-axis ( $\mu_5$  as well as  $\mu_6$ ) contribute independently to the wavenumber, and a model with  $R_z > R$  and  $\mu_z < \mu$  (using an index Z as a common term for both of the positions 5 and 6), is therefore in complete agreement with the wavelength ratio found experimentally.

According to this model the tetrammine cupric ion in aqueous solution should contain 2 water molecules. The absorption curve for this ion is more symmetrical than for the homogeneous complexes (see Fig. 3), and the analysis of the spectrum in this case does not permit conclusions to be drawn about the second band, the intensity of which seems to be small.

When the di-aquo tetrammine ion exchanges one of its water molecules with an ammonia molecule there is an anomalous shift of  $\lambda_1$  towards the red (the so-called "pentammine effect"), but a similar effect is not found with the uptake of the 6th ammonia molecule. It is very remarkable that the pentammine spectrum — estimated from rather dilute ammonia solutions — is but little different from the spectrum of cupric nitrate in liquid ammonia (compare the absorption curve for  $\text{Cu am}_N^{++}$  in Fig. 3 with the curve for  $\text{Cu am}_5^{++}$  in Fig.

4). How can this be explained? J. Bjerrum<sup>14,20</sup> has maintained that it does not give much evidence for the existence of a hexammine complex, and later<sup>29,30</sup> has tried to prove that the cupric ion in solution cannot exceed the coordination number 5. However, in the picture of the theory developed here the missing hexammine effect can be explained by assuming that the effective dipole moments for the last water molecule and the 6th ammonia molecule are nearly equal, and for this reason give the same contribution to the wave number. The permanent dipole moment for water is higher than that for ammonia, but the polarizability of the latter molecule is higher, and this causes the average effective dipole moments to be essentially higher for ammonia than for water ligands (*cf.* Table 2). For the 6th ammonia molecule we may also assume for thermodynamic reasons that  $\mu_6(\text{NH}_3) \sim \mu_6(\text{H}_2\text{O})$ , as seen by the following consideration. The decrease in free energy resulting from the uptake of the 6th ammonia molecule is formally given by

$$-\Delta G_6 = \frac{q \cdot \Delta \mu_6}{R^2 \cdot D}, \quad (2)$$

where  $q$  is the charge of the cupric ion,  $\Delta \mu_6 = \mu_6(\text{NH}_3) - \mu_6(\text{H}_2\text{O})$ , and  $D$  the effective dielectric constant.

The intensity of the absorption band in liquid ammonia is about 10 % higher than that of the pentammine band (see Fig. 4), and it can be estimated that the average ligand number  $\bar{n} = 5.5$  is first reached when the mole fraction of ammonia is about 0.35 — 0.40. This shows directly that water and ammonia compete on equal terms for the 6th and last position in the configuration assumed, thus giving thermodynamic support for  $\Delta \mu_6 \sim 0$ . Referring to molar concentrations in water ( $a_{\text{H}_2\text{O}} \lesssim 1$ ), the 5th consecutive formation constant  $K_5$  is about 1/3, and it was earlier postulated<sup>14,p.109</sup> that  $K_6$  is at least 200 times smaller. A closer consideration of the spectra previously recorded makes it probable that we have  $K_5/K_6 \sim 100$ , but this ratio is still considerably higher than the statistically expected value of 4.

It is possible to get some information on the extent to which the tetragonal bipyramidal model deviates from the regular octahedral configuration. The stronger the electric field the closer a given ligand is pulled nearer to the central ion and the greater must be the fraction of  $\mu$  due to the polarization; we must therefore expect that if  $R < R_z$ , then  $\mu > \mu_z$ . Using this postulate a closer examination of the model shows that in order to obtain the experimentally determined wavenumbers for the hexaquo and hexammine spectra,  $\nu_1/\nu_2 = 1.33$  and  $R \sim 2 \text{ \AA}$ ,  $R_z$  cannot exceed  $R$  by more than about 8 % if the dipole moments of the ligands bound at the four positions in the square (see Fig. 1) are to be higher than the dipole moments of the ligands placed at the positions 5 and 6 along the Z-axis. This result is utilized in Table 3 where  $\mu$  and  $\mu_z$  are calculated from the wavenumbers of the hexaquo and hexammine ions for  $R = 1.95$  and  $2.00 \text{ \AA}$ , respectively, selecting values for  $R_z$  a few per cent higher than  $R$ . The ratios  $\frac{\Delta \mu}{R^2}$  and  $\frac{\Delta \mu_z}{R_z^2}$  are similarly tabulated, giving a rough measure of the tendency of water to exchange with ammonia in the square and perpendicular to the square. The pentammine effect defined

Table 3. Results of calculations with the tetragonal bipyramidal model of copper (II)-ion dipole complexes.

Dipole moments and pentammine effect  $\Delta\lambda_1 = \lambda_1(\text{Cu am}_5) - \lambda_1(\text{Cu am}_4)$  as function of the distances  $R$  and  $R_z$ .  $\Delta\lambda_1(\text{exp.}) = 50m\mu$ .

Ligand	$R$ (Å)	$R_z$ (Å)	$\mu$ (Debye)	$\frac{\Delta\mu}{R^2}$	$\mu_z$ (Debye)	$\frac{\Delta\mu_z}{R_z^2}$	$\Delta\lambda_1(m\mu)$
H <sub>2</sub> O	1.95	2.00	5.12	0.324	3.74	0.222	55
NH <sub>3</sub>	»	»	6.35		4.63		
H <sub>2</sub> O	1.95	2.05	5.07	0.328	4.05	0.231	55
NH <sub>3</sub>	»	»	6.32		5.02		
H <sub>2</sub> O	2.00	2.05	5.79	0.396	4.35	0.242	85
NH <sub>3</sub>	»	»	7.37		5.37		
H <sub>2</sub> O	2.00	2.20	5.65	0.338	6.23	0.304	35
NH <sub>3</sub>	»	»	7.00		7.70		

as  $\Delta\lambda_1 = \lambda_1(\text{Cu am}_5) - \lambda_1(\text{Cu am}_4)$  is also given, and Table 3 shows that the calculations made give a pentammine effect of the right order of magnitude ( $\sim 50 m\mu$ ). This is a remarkable result since an effect of this kind will manifest itself only in the cases where the ligands are not equivalently bound. The final choice of the parameters was taken as  $R = 1.95$  Å, and  $R_z = 2.00$  Å, a pair of distances giving nearly the right pentammine effect, and for which the ratio

$\frac{\Delta\mu}{R^2} : \frac{\Delta\mu_z}{R_z^2}$  is found to be  $\sim 1.5$ . The ratio of the affinities estimated from the complexity constants are considerably higher, but a quantitative agreement cannot be expected.

The interesting result that the Cu(II)-complexes seem to deviate only slightly from regular octahedral configuration agrees well with X-ray diagrams of crystalline hexammine cupric bromide taken at room temperature with a 19 cm Bradley-Jay camera using CuK $\alpha$ -radiation in Haldor Topsøe's Laboratories by J. Rathlev. In complete agreement with Peyronel<sup>21</sup> this salt was found to have a cubic face centered structure.

The reflection spectra of crystalline CuSO<sub>4</sub>·5 H<sub>2</sub>O and of anhydrous CuSO<sub>4</sub> have been measured for us in the laboratory of F. L. Smith and Co. by K. A. Simonsen; the spectra are plotted in Fig. 5. It will be seen that the colourless CuSO<sub>4</sub> has a reflection spectrum in the near infrared only slightly displaced relative to the spectrum of the blue hydrate. The oxygen in the sulphate groups has nearly the same polarizability as water, and this explains why the maximum of reflection of the crystalline hydrate is situated at the same wavelength as the absorption maximum of the hexaquo cupric ion in solution (*cf.* Fig. 2). The structure of anhydrous CuSO<sub>4</sub> is unknown, but it is assumed that the spectrum is due to the influence of the oxygen groups.

Thus the chemical facts and the theoretical considerations seem to verify the proposed constitution of the hexaquo cupric ion and analogous Cu(II)-complexes.

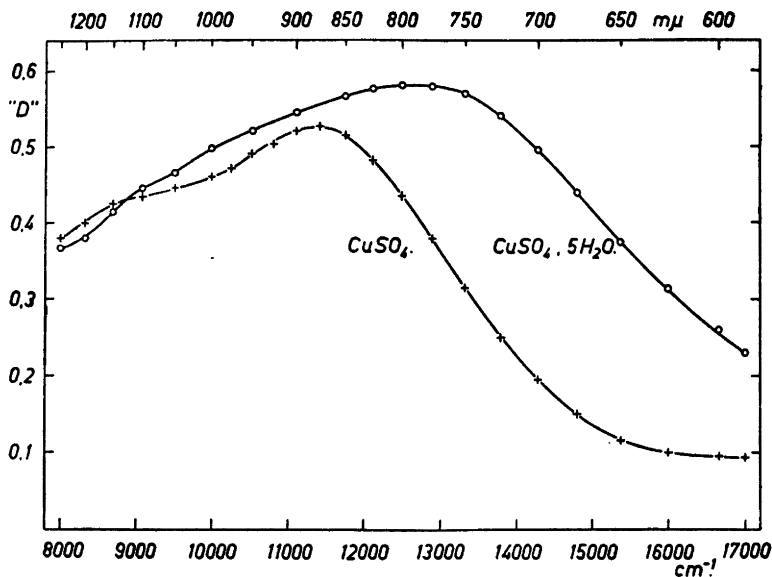


Fig. 5. Reflection spectra of cupric sulphate, anhydrous and pentahydrate. Measurements with the reflection spectrum attachment of the Beckman DU spectrophotometer by K. A. Simonsen (the optical density 'D' is only a relative measure for the light absorbed).

#### RESULTS WITH MORE UNSYMMETRICAL COMPLEXES

J. Bjerrum<sup>19</sup> has estimated the spectra of the intermediate complexes  $\text{Cu am}_n^{++}$  for  $n = 1, 2, 3$  and 4 by resolving the mixed spectra of equilibrium solutions for values of  $\bar{n}$  varying from 0 to  $\sim 5$ . Using the ideas outlined in the preceding sections it is also possible to calculate the wavelength of the band maxima of these complexes. The calculations are more tedious to perform than in the previous cases, since the symmetry of the field is lower. This causes the original five-fold degeneracy of the ground level to be removed to a higher degree. The mixed complexes are, therefore, supposed to have three or four bands, the first two of which, according to the theory, are placed adjacently. For statistical reasons (*cf.* Ref. 14, pp. 43, 109) the first four ammonia molecules must occupy the positions 1—4 in Fig. 1, and as before it was assumed that the distances  $\text{Cu-NH}_3$  and  $\text{Cu-H}_2\text{O}$  are equal. The complete calculations will be published by C. J. Ballhausen and only the results are quoted here. If the chosen values of the parameters  $R$  and  $R_z$ ,  $\mu$  and  $\mu_z$ , are inserted in the derived expressions we get remarkable agreement with the experimental values for the bands of highest frequency, as shown in Table 4.

Only one of the intermediate complexes, the diammine cupric ion, should exist in a *cis* and a *trans* form, and it is of considerable interest that the computations give some information on this point. The theory implies that the

Table 4. Comparison of calculated and experimental values of the wavelength of the band of highest frequency in the series of cupric ammine complexes.

Values of the parameters used in the calculation:

$$R = 1.95 \text{ \AA}, \quad \mu(\text{H}_2\text{O}) = 5.12 \text{ D.}, \quad \mu(\text{NH}_3) = 6.35 \text{ D.}$$

$$R_Z = 2.00 \text{ \AA}, \quad \mu_Z(\text{H}_2\text{O}) = 3.74 \text{ D.}, \quad \mu_Z(\text{NH}_3) = 4.63 \text{ D.}$$

Formula of complex	$\lambda_1$ (m $\mu$ )	$\lambda_1$ (m $\mu$ )
	calculated	experimental
$\text{Cu}(\text{H}_2\text{O})_4, (\text{H}_2\text{O})_2^{++}$	—	790
$\text{Cu}(\text{NH}_3)(\text{H}_2\text{O})_3, (\text{H}_2\text{O})_2^{++}$	710	745
<i>cis</i> - $\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_2, (\text{H}_2\text{O})_2^{++}$	670	680
<i>trans</i> - $\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_2, (\text{H}_2\text{O})_2^{++}$	620	~600
$\text{Cu}(\text{NH}_3)_3(\text{H}_2\text{O}), (\text{H}_2\text{O})_2^{++}$	660	645
$\text{Cu}(\text{NH}_3)_4, (\text{H}_2\text{O})_2^{++}$	(590)	590
$\text{Cu}(\text{NH}_3)_4, (\text{NH}_3)(\text{H}_2\text{O})^{++}$	—	640
$\text{Cu}(\text{NH}_3)_4, (\text{NH}_3)_2^{++}$	—	640

maximum of the experimental curve for the diammine complex at 680 m $\mu$  is a *cis* band by analogy with the band of the mono-ethylenediamine complex (see Fig. 6), which necessarily is that of a *cis* spectrum. The theory further predicts the situation of a *trans* band for the diammine ion at ~620 m $\mu$ . After the calculations had been performed, evidence for such a band was found near 600 m $\mu$  by a careful examination of Bjerrum's<sup>19</sup> original curve for the diammine spectrum. The equilibrium is probably displaced strongly in favour of the *cis* ion in this case (*cf.* Bjerrum and Rasmussen<sup>36</sup>). The *trans* band is more pronounced in the computed spectrum of the dipyridino complex, the three spectra discussed being drawn for comparison in Fig. 6.

The spectra so far discussed are all atomic. In addition to their atomic spectra in the red and infrared many acido copper(II) complexes, *e. g.* the chloro cupric complexes<sup>37</sup>, have very high absorption bands in the ultraviolet,

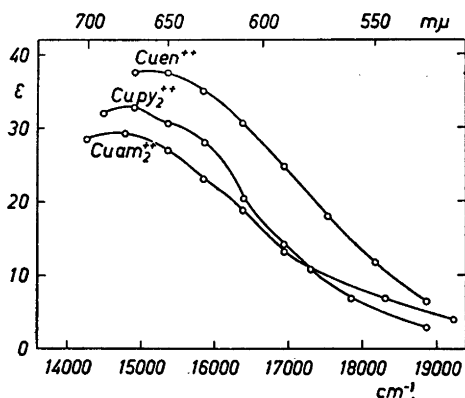


Fig. 6. Comparison of spectra of diammine cupric ions. Curves for the diammonia complex (see Fig. 4), for the mono-ethylenediamine complex<sup>29</sup>, and for the dipyridino complex (unpublished result<sup>29</sup>). The mixed spectra of cupric nitrate pyridine solutions in 0.5 M pyridinium nitrate were resolved by the method of least squares.

which are probably molecular spectra due to polarization of the ligands. Winther<sup>38</sup> and Ley<sup>39</sup> have demonstrated ultraviolet absorption by  $\text{CuSO}_4$ -ammonia solutions, especially if they are poor in ammonia. The intensity of the band is approximately inversely proportional to the concentration of ammonium ions (at least in the range 0.1—0.8  $M$   $\text{NH}_4\text{ClO}_4$  for solutions having  $[\text{NH}_3] \sim 0.1 M$ ). Further, Kirson<sup>40</sup> has shown that the catalytic influence of cupric ammonia solutions on the decomposition of hydrogen peroxide also varies inversely with the ammonium concentration. The ultraviolet absorption disappears in strong ammonium salt solutions, and we must therefore conclude that it is due to the formation of hydroxo complexes, as *e. g.*  $[\text{Cu}(\text{NH}_3)_3(\text{OH})(\text{H}_2\text{O})_2]^+$ . The concentrations of hydroxo complexes cannot be very high, since they do not noticeably disturb the ammine formation in 0.5—5  $M$  ammonium nitrate solutions<sup>14,p.125</sup>.

#### REMARKS ON THE THEORY

It is rather unexpected that a first order approximation using but few parameters is able to describe the spectra of such complex systems. In the foregoing sections the parameters have been chosen in such a way that the experimental facts are explained. But we wish to point out that the parameters (the effective charge  $Z$  and the dipole moment  $\mu$ ) used here do not necessarily correspond directly to any physical reality, and they should not be used uncritically in other connections.

The theory predicts sharp lines, but in fact, bands are observed. An explanation of this fact may be found in the oscillations of the dipole ligands in the potential hole of the equilibrium positions. These oscillations affect the energy of the system, which is very sensitive to changes in  $R$ . The energy differences between the levels are, therefore, not very constant, and as the frequency of the electron is about 1 000 times the frequency of the oscillating dipole, it is reasonable to assume that the broadening of the bands is a statistical effect due to light absorption by all the complex ions in the solution. The total broad absorption curves thus produced are nearly symmetrical and, as experiments show, have approximately the shape of an error-curve. The bands are also sensitive to variations in temperature; by lowering the temperature they all show hypsochromic effects. This is perhaps explained as a consequence of temperature lowering drawing the ligand closer to the cation thus increasing the perturbation.

In those cases where the energy differences are not very dependent on the oscillations of the ligands, the bands do not broaden much. This is the case with the absorption spectra of the rare earths (when the crystal field has nearly no influence at all), and *e. g.* with a narrow band of the chromium-(III) ion near 670  $m\mu$ <sup>41</sup>.

It is a result of the above discussion that the spectra of the copper(II)-ammines in aqueous solution can be described without assuming overlap forces between the ligand and the cation. However, in the total description of a complex ion we must take electron exchange into account; the number and sites of the ligands is at least partly due to such an effect. On the other hand, our calculations show that when we take, for example, a cupric ion, and sur-

round it with four ligands, then the ground energy level of the complex resulting both from the perturbations and the electrostatic forces will be lower in a planar configuration than in a tetrahedral one. Thus both the crystal-field theory and the hybridization theory predict that in a cupric complex with coordination number 4 the ligands will be placed square planar.

In later papers it will be shown that the spectra of all the transition group elements can be explained along these lines using the theories of Bethe<sup>10</sup> applied to an intermediately strong crystal field. It also seems possible that the magnetic and kinetic properties of, *e. g.*, the hexammine cobalt(III) ion and other complex ions, can be explained by this theory, as has been pointed out in special cases by Orgel<sup>24</sup>.

## REFERENCES

1. Luther, R. and Nikolopoulos, A. *Z. physik. Chem.* **82** (1913) 361.
2. Fajans, K. *Naturwiss.* **11** (1923) 165.
3. Mead, A. *Trans. Faraday Soc.* **30** (1934) 1052.
4. Kato, S. *Sci. Papers Inst. Phys. Chem. Research* **13** (1930) 49.
5. Bose, D. M. and Mukherji, P. C. *Phil. Mag.* [7] **26** (1938) 757.
6. Shibata, Y. *Spectrochemistry I*. Tokyo 1935.
7. Tsuchida, R. *J. Chem. Soc. Japan* **13** (1938) 388, 436, 471.
8. Linhard, M. and Weigel, M. *Z. anorg. Chem.* **266** (1951) 49.
9. Ilse, F. E. and Hartmann, H. *Z. physik. Chem.* **197** (1951) 239.
10. Bethe, H. *Ann. Physik* [5] **3** (1929) 133.
11. Penney, W. G. and Schlapp, R. *Phys. Rev.* **41** (1932) 194; **42** (1932) 666.
12. Ilse, F. E. and Hartmann, H. *Z. Naturforschg.* **6a** (1951) 751.
13. van Vleck, J. H. *Phys. Rev.* **41** (1932) 208.
14. Bjerrum, J. *Metal ammine formation in aqueous solution*. Copenhagen 1941.
15. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **11** (1931) No. 5, p. 20.
16. Irving, H. and Williams, R. J. P. *J. Chem. Soc.* **1953** 3205.
17. Bjerrum, N. and Kirschner, Aa. *Kgl. Danske Videnskab. Selskab Skr.* [8] **5** (1918) No. 1.
18. Rosenblatt, F. *Z. anorg. Chem.* **204** (1932) 351.
19. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **11** (1932) No. 10.
20. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **12** (1934) No. 15.
21. Peyronel, G. *Gazz. chim. ital.* **71** (1941) 363.
22. Iü, S. H. and Beevers, C. A. *Z. Krist. A* **95** (1936) 426.
23. West, C. D. *Z. Krist. A* **91** (1935) 480.
24. Orgel, L. E. *J. Chem. Soc.* **1952** 4756.
25. Beevers, C. A. and Lipson, H. *Proc. Roy. Soc. London A* **146** (1934) 570.
26. van Niekerk, J. N. and Schoenig, F. R. L. *Acta Cryst.* **6** (1953) 227.
27. Biltz, W., Bröhan, H. and Wein, W. *Z. anorg. Chem.* **148** (1925) 207.
28. Nyholm, R. S. *Chem. Revs.* **53** (1953) 263.
29. Bjerrum, J. and Nielsen, E. J. *Acta Chem. Scand.* **2** (1948) 297.
30. Bjerrum, J. and Lamm, C. G. *Acta Chem. Scand.* **4** (1950) 997.
31. Jørgensen, Chr. *Klxbüll Acta Chem. Scand.* **8** (1954) 175.
32. Slater, J. C. *Phys. Rev.* **36** (1930) 57.
33. Jensen, A. Tovborg, *Krystallinske Salhydrater*, Thesis, Copenhagen 1948.
34. Schuyer, J. *Rec. trav. chim.* **72** (1953) 933.
35. van Santen, J. H. and van Wieringen, J. S. *Rec. trav. chim.* **71** (1952) 420.
36. Bjerrum, J. and Rasmussen, S. E. *Acta Chem. Scand.* **6** (1952) 1265.
37. Doehlemann, E. and Fromherz, H. *Z. physik. Chem. A* **171** (1934) 371.
38. Winther, Chr. and Mynster, E. H. *Z. wiss. Phot.* **24** (1926) 90.
39. Ley, H. *Z. anorg. Chem.* **164** (1927) 392.
40. Kirson, B. *Bull. soc. chim. France* **1952** 957.
41. Deutschbein, O. *Ann. Physik* [5] **14** (1932) 753.

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