Spectrochemical Study of Microscopic Crystals. XXIII[1]. *The Structure and Light Absorption of Red Cupric Complexes with Succinimide*[2]

By Shoichiro YAMADA and Seiko MIKI

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Succinimide readily loses a proton and is combined, in the anionic form, with various metal ions. There have been reported a number of cupric compounds with succinimidate anions, which are red or violet in the solid state and many of which change their color from red in the crystalline state to deep-blue in some solvents. On one hand, the formation of the red compounds of copper(II) is interesting, since it is well known that most quadri-co-ordinate cupric complexes are blue, green or violet; red cupric complexes, therefore, are rather unusual examples. On the other hand, the color change from the solid to the solution, as observed with these complexes, is so remarkable that the study of this phenomenon is thought to be interesting from the viewpoint of the co-ordination chemistry of cupric complexes. The present work was undertaken both in order to elucidate the structure of these and relevant compounds and in order to discuss the origin of the red color of the cupric compounds in terms of the stereochemistry and bonding involved.

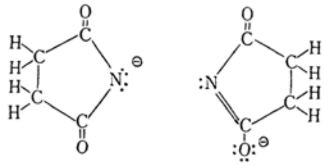

Fig. 1. Succinimidate ion.

Experimental

Materials.—Bis(succinimidato)diammine-copper(II) was obtained as pink crystals from copper powder, succinimide and aqueous ammonia by the method of Tschugaeff[3], using ethanol as a solvent. The compound is insoluble in organic solvents.

Bis(succinimidato)bis(alkylamine)-copper(II) complexes with methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl and *n*-amyl amines, which had also been reported previously by Tschugaeff, were prepared as pink crystals according to the directions in the original report. Purification of the compounds was carried out by recrystallization from ethanol containing an excess amount of the free amines, as had also been reported in a previous paper[3].

All these compounds have the formula of $Cu\cdot(sucim)_2(amine)_2$, except for the compound with ethyl amine, which contains two water molecules of crystallization[4]. The crystals are stable in the air at room temperature when completely free from the solvent. The crystals are not stable in water, methanol, ethanol, dioxan or pyridine. It has been found in the present work that the red crystals of the compounds are soluble and stable enough in non-co-ordinating solvents, such as chloroform, methylene chloride and benzene, to form a dark-blue solution; an exception is the compound with methyl amine, which is readily soluble in chloroform but sparingly soluble in methylene chloride and benzene. The stability of the red complexes seems to increase as the chain of the alkyl group becomes longer.

Potassium tetrakis(succinimidato)copper(II) hexahydrate was prepared as pink crystals according to the method of Tschugaeff[5].

The sample of bis(*N,N*-diethylethylenediamine)-copper(II) perchlorate, which is colored pink in the crystalline state and deep-blue in an aqueous solution, was kindly supplied by Dr. Hisao Ito of the medical department, to whom the present authors are grateful.

Measurements.—The dichroism in the visible and ultraviolet regions was determined by Tsuchida and Kobayashi's microscopic method[6] using polarized light on the well-developed faces, which are shown in the figures. The ultraviolet absorption spectra of the compounds in solution were determined with a Beckman DU spectrophotometer. The notations in the present paper are the same as those used in the former papers of this series.

Results and Discussion

The Absorption Spectrum of Potassium Tetrakis(succinimidato)cuprate(II) Hexahydrate.—It is possible that the succinimidate ion in $K_2Cu\cdot(sucim)_4\cdot 6H_2O$ is co-ordinated to the cupric ion through either the nitrogen or the oxygen

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[1] Part XXII of this series; S. Yamada, H. Nishikawa and R. Tsuchida, This Bulletin, 33, 1278 (1960).

[2] Presented in part at the Symposium of Co-ordination Chemistry, Osaka, November, 1961.

[3] L. Tschugaeff, *Ber.*, 39, 2897 (1905).

[4] The notation, *sucim*, represents an anion which is derived when a succinimide molecule loses a proton.

[5] L. Tschugaeff, *Ber.*, 40, 1976 (1907).

[6] R. Tsuchida and M. Kobayashi, This Bulletin, 13, 619 (1938); "The Color and the Structure of Metallic Compounds" (Kinzokukagōbutsu no Iro to Kōzō), Zoshindo, Osaka (1944), p. 180.

atom (Fig. 1). The co-ordination of *sucim* with a copper(II) ion, however, is most probably, through the nitrogen atom, since the oxygen atom of the carbonyl group in the ion is capable of being linked only weakly with the cupric ion. The co-ordination of *sucim* as a chelated ligand using both the nitrogen and the oxygen atoms may not be impossible. In any case, the bonding is mainly through the nitrogen atom, judging from the steric condition and the weak bonding ability of the oxygen atom in the carbonyl group.

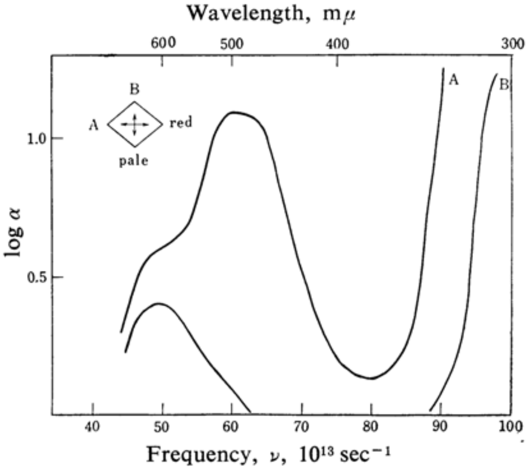

Fig. 2. Polarized absorption spectra of $K_2Cu\cdot(sucim)_4\cdot 6H_2O$ in the crystalline state.

TABLE I. ABSORPTION MAXIMA OF $K_2Cu(sucim)_4\cdot 6H_2O$ IN THE CRYSTALLINE STATE

	ν_{max}	log α	Half width	Assignment
A-abs.	61.2	1.08	12.5	ν_2
	ca. 50	—	—	ν_1
B-abs.	ca. 50	0.40	ca 11	ν_1

ν; 10^{13} sec^{-1}

The polarized absorption spectra of $K_2Cu\cdot(sucim)_4\cdot 6H_2O$ in the crystalline state are shown in Fig. 2, and the data are given in Table I. The free succinimide shows no absorption in the neighborhood of the ligand field bands of the cupric complexes⁷⁾. Since the crystal structure analysis is not available, it is not possible to determine exactly the components of the absorption coefficient of the planar cupric complex. For the purposes of the present study, however, it is sufficient to find the qualitative characteristics of these absorption components. It is known empirically from dichroism measurements⁸⁾ that, for the ligand field absorption band of cupric complexes with the D_{4h} symmetry, the xy-absorption, the absorption with the electric vector along the $Cu(N)_4$-plane, has a much larger oscillator strength than the z-absorption, the absorption with the electric vector perpendicular to the complex-plane. On the basis of this empirical rule, it is found that the A-absorption in Fig. 2 is richer with the xy-absorption than with the z-absorption of the planar complex, and that the B-absorption is richer with the z-absorption. The difference between the A- and the B-absorption on this crystal-face is so remarkable, compared with the dichroism of other cupric complexes, that one may assume that the $Cu(N)_4$-planes are nearly parallel to each other and perpendicular to the B-direction of the crystal.

The compound shows its main ligand field band at about 61×10^{13} sec^{-1}, which corresponds to a much higher frequency than the values reported for an ordinary type of cupric complex with amines, such as ammonia and ethylenediamine. An inspection of data with nickel(II)-succinimidato complexes having the same configuration reveals⁹⁾ that the position of *sucim* in the spectrochemical series is as follows¹⁰⁾: *en* > NH_3 > biguanide > *sucim* > OH_2. This order, in which *en* stands higher than *sucim*, is regarded as applicable to many metal ions, such as chromium(III), nickel(II), cobalt(II), cobalt(III), and copper(II), provided that the complexes have the same configuration. Hence, the fact that the tetrakis(succinimidato)-copper(II) ion shows its absorption band at such a high frequency is not understandable if $K_2Cu(sucim)_4\cdot 6H_2O$ has a complex-ion with a configuration identical with that of the bis(ethylenediamine)copper(II) complexes. Bjerrum¹¹⁾ et al. and Ito¹²⁾ concluded that the ligand field band of copper(II) suffered bathochromic shift as the cupric complex with a square-planar configuration took additional ligands to form a sexa-co-ordinate complex with a pseudo-octahedral configuration. Taking this and the spectrochemical series into consideration, a comparison of the maxima of the ligand field bands indicates that the co-ordination of the four nitrogen atoms around the cupric ion in $K_2Cu(sucim)_4\cdot 6H_2O$ is square-planar, the fifth and sixth positions of the complex being unoccupied, whereas the ethylenediamine complex has a sexa-co-ordinate configuration, represented

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7) L. J. Saidel, *Nature*, **172**, 955 (1953).

8) S. Yamada and R. Tsuchida, *Ann. Reports Faculty of Sci., Osaka Univ.*, **4**, 79 (1956); This Bulletin, **29**, 289, 694 (1957).

9) S. Yamada and H. Nishikawa, to be published.

10) The notation, *en*, represents a molecule of ethylenediamine.

11) J. Bjerrum, C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

12) H. Ito, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1395 (1956).

by $[Cu\,en_2\,(OH_2)_2]^{2+}$. In other words, it is concluded that $K_2Cu(sucim)_4 \cdot 6H_2O$ contains a square-planar complex-ion, $[Cu(N)_4]^{2-}$, which leaves the fifth and sixth co-ordination sites empty, the water molecules in this compound being unbound with the cupric ion.

Some of the reasons why the complex-ion, $[Cu(sucim)_4]^{2-}$, leaves the fifth and sixth sites unoccupied seem to be (1) that the steric condition more or less, though not absolutely, prevents other ligands from coming close to the cupric ion and (2) that the oxygen atom in the carbonyl group has only a weak ability to be bound with the cupric ion. Another factor is the electronic state of the ligands, which will be discussed in the later part of this paper.

A similar discussion applies to the corresponding complex of biuret, which involves a chemical bond resembling the bond in the complex of succinimide. It seems to be significant that the position of the biuret ion in the spectrochemical series is close to that of *sucim*. The absorption maximum (505 mμ)[13] of the crystal of $K_2Cu(biuret)_4 \cdot 4H_2O$ also lies at a much higher frequency than that of the ethylenediamine-complex of copper(II). In the same way as in the case of $K_2Cu(sucim)_4 \cdot 6H_2O$, the inspection of the absorption maxima shows that the crystal consists of $[Cu(biuret)_2]^{2-}$ ions which have a square-planar co-ordination around the cupric ion, with the fifth and sixth co-ordination sites left empty, the water molecules being unbound with the cupric ion. This is in agreement with the crystal structure analysis[13] of the compound, which shows that the cupric ion is surrounded by four nitrogen atoms at a distance of about 1.93 Å and by two nitrogen atoms of the neighboring complex at about 3.33 Å.

It is theoretically predicted that the quadri-co-ordinate cupric complex of the D_{4h} field symmetry will display three ligand field bands, as shown in Fig. 3. There are two ways of assigning these vibronic transitions. According to one of them, the three transitions all fall in a rather narrow frequency range and the superposition of the three usually appears as apparently one absorption band in the visible or near-infrared region. According to the other way of assignment[14], the ν_3 band is assumed to lie at a much higher frequency than ν_1 and ν_2, and usually far from the visible region, covered by a much stronger absorption of a charge transfer type. The present authors regard the latter assignment as more likely on grounds, a detailed discussion of which will be reported shortly. The present dichroism measurements also seem to support this assignment.

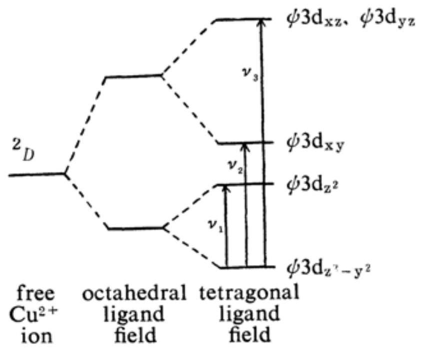

Fig. 3. Energy level scheme model for cupric complexes: (A) sexa-co-ordinate complexes with octahedral symmetry and (B) square-planar complexes of a $[Cu\,A_4]$ type. In the figure, $\phi 3d_{z^2}$, for example, refers to the state, in which the d_{z^2} orbital is not completely filled.

As may be seen in Fig. 2, $K_2Cu(sucim)_4 \cdot 6H_2O$ shows two maxima, corresponding to the ligand field bands, at about 50 and 61×10^{13} sec^{-1}, for both of which the xy-absorption is more intense than z-absorption. An unambiguous assignment of the observed transitions seems to be difficult for the present, but a tentative assignment is given in Table I on the basis of the dichroism measurement and in terms of the second standpoint described above. Simple theoretical consideration, in terms of the ligand field theory, predicts that both the transitions, ν_1 and ν_2, will take place more readily along the xy-direction than along the z-direction, if it is assumed that the vibrations of the E_u symmetry are more effective in making allowed the originally forbidden electronic transitions than the other vibrations in the complex (Table II). The energy levels of the d_{z^2} and d_{xy} orbitals are usually close to each other, and the order of one with respect to the other

TABLE II. THE TRANSITIONS CORRESPONDING TO THE LIGAND FIELD BANDS OF SQUARE-PLANAR COMPLEXES OF [Cu A$_4$]-TYPE AND THE SYMMETRIES OF THE VIBRATIONS MAKING THE TRIPLET-TRIPLET TRANSITIONS ALLOWED

Transition	Polariz. of transition predicted from symmetry consideration
ν_1 $d_{z^2} \rightarrow d_{x^2-y^2}$	$x, y(E_u)$; $z(B_{2u})$
ν_2 $d_{xy} \rightarrow d_{x^2-y^2}$	$x, y(E_u)$; $z(B_{2u})$
ν_3 $\left.\begin{matrix} d_{xz} \\ d_{yz} \end{matrix}\right\} \rightarrow d_{x^2-y^2}$	$x, y(A_{2u}, B_{2u})$; $z(E_u)$

In the parentheses are shown the vibrations of the complex making the transition allowed.

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[13] H. C. Freeman, J. E. W. L. Smith and J. C. Taylor, *Acta Cryst.*, **14**, 407 (1961).

[14] D. P. Graddon, *J. Inorg. Nucl. Chem.*, **7**, 73 (1958).

possibly changes from one compound to another. The assignment, as given in the present work, is based upon the order of the d-orbitals assumed in Fig. 3. Irrespective of the order of the two levels, the polarization which has been determined in the present work is found to agree with the prediction from the theory, at least qualitatively.

The Absorption Spectrum of Bis(*N, N*-diethylethylenediamine)copper(II) Perchlorate. — The compound consists of complex-ions of a $[Cu(N)_4]$-type with a square-planar configuration. The two ethyl groups attached to a nitrogen atom prevent, to a greater or lesser extent, additional ligands from occupying the fifth and sixth co-ordination sites, although in an aqueous solution the complex takes up two molecules of water to form a sexa-co-ordinate complex. The polarized absorption spectra of the compound in the crystalline state are shown in Fig. 4. The crystal structure analysis of the complex salt is not available so far, and usually the planes of the complexes in the crystal are not exactly parallel to each other. However, it is readily found that the A- and B-absorptions in Fig. 4 represent the main features of the xy-absorption and the z-absorption respectively of the square-planar complex, since previous studies have shown that, for the ligand field absorption band, the xy-absorption has a larger oscillator strength than the z-absorption⁸⁾. Strictly speaking, the symmetry of the complex deviates from D_{4h}, but the spectra may be discussed approximately in the scheme of the D_{4h} field symmetry. The absorption bands in the visible region in Fig. 4 probably represent a superposition of the two kinds of electronic transitons, ν_1 and ν_2. A tentative assignment of the band which is shown in Table III is made in such a way that the assignment for the compound is consistent with the assignment for the $[Cu\cdot(sucim)_4]^{2-}$ ion and other square-planar cupric complexes.

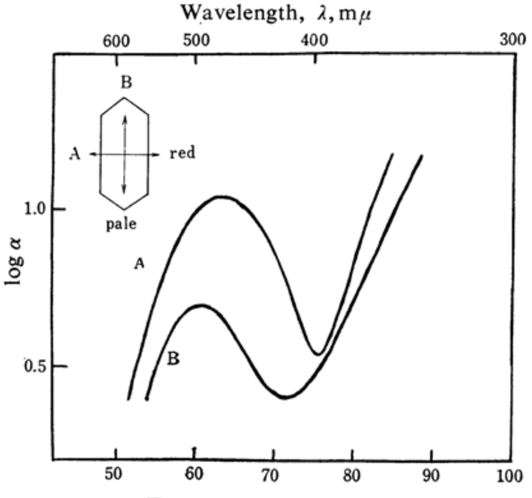

Fig. 4. Polarized absorption spectra of $[Cu\cdot(deen)_2](ClO_4)_2$ in the crystalline state.

TABLE III. ABSORPTION MAXIMA OF $[Cu(deen)_2](ClO_4)_2$

Crystal	ν_{max}	log ε	Half width	Assignment
A-abs.	63.4	1.04	18.8	ν_1, ν_2
B-abs.	60.0	0.70	13.6	ν_1
Solution[a]	ν_{max}	log ε		
	50.6	1.18		

ν; 10^{13} sec⁻¹

a) H. Ojima and K. Sone, This Bulletin, **35**, 298 (1962).

An absorption band in the visible region in the A-absorption is assumed to consist of two electronic transitions, since the band is comparatively broad. The B-absorption shows only one ligand field band at about 61×10^{13} sec⁻¹, which probably arises from the electronic transition, ν_1. As is seen in Table III, the polarization observed for these transitions is found to agree with the prediction from the theory.

It is to be noted that the absorption maximum of the square planar ion of $[Cu(deen)_2]^{2+}$ lies at a much higher frequency than the maximum of $[Cu\,en_2(OH_2)_2](NO_3)_2$ in the crystalline state (57.2×10^{13} sec⁻¹) and that of $Cu\,en_2{}^{2+}$ (54.0×10^{13} sec⁻¹) and $Cu(NH_3)_4{}^{2+}$ (49.2×10^{13} sec⁻¹) ions in an aqueous solution. The difference in the maximum frequency between the crystalline $[Cu(deen)_2](ClO_4)_2$ and the latter type of complex is too large to be expected if the two contain complexes of a similar configuration, since the position of *deen* in the spectrochemical series is close to, and even lower than, en. This fact is understood if it is assumed (1) that the co-ordination of ligands at the fifth or the sixth site causes a bathochromic shift of the ligand field band, and (2) that bis(ethylenediamine)- or tetrammine-copper(II) ions in solution and in the crystalline state consist of complex-ions of copper(II), with the fifth and the sixth co-ordination sites occupied by some ligands.

The ligand field band of bis(*N, N*-diethylethylenediamine)-copper(II) perchlorate exhibits a great bathochromic shift on going from the square-planar complex, $[Cu(N)_4]^{2+}$, in the solid state to the trans-octahedral complex, $[Cu(N)_4(OH_2)_2]^{2+}$, in an aqueous solution. The following ratio obtains in this case:

$$\nu(\text{trans-octahedr.})/\nu(\text{square-plan.})=0.80$$

This value is nearly comparable with the values previously reportd for some cupric complexes[15]. In this connection, it is to be noted that bis(ethylenediamine)copper(II) perchlorate in the crystalline state shows a ligand field band at a comparatively long wavelength[16]. One may assume that the perchlorate ions come rather close to the copper(II) ion to form a sexa-co-ordinate complex, giving rise to the bathochromic shift of the band. The study of this is now in progress and will be reported elsewhere in more detail.

The Origins of the Red Color of Cupric Complexes.—There seem to be largely two kinds of origins of the red or orange color of some cupric compounds. On one hand, the red color results mainly from the charge transfer between the cupric ion and a ligand, and, on the other hand, it originates from the ligand field bands of the cupric ion. Red halide-complexes of copper(II) belong to the former group, owing their red color to a charge transfer between cupric and halide ions. The orange-color of Cs_2CuCl_4 and the red-color of $CsCuCl_3$, for example, are regarded as due to the charge transfer band in the visible region, which is much more intense than the ligand field band. In addition to the charge transfer band, the ligand field band due to the tetrahedral copper(II)-complex is expected to appear in the infrared region.

There are red cupric complexes of the other type, such as cupric complexes with succinimide, biuret, biguanide, phenylbiguanide, and *N, N*-diethylethylenediamine (Table IV). The quadri-co-ordinate, planar complex of copper(II) tends to take additional ligands, forming a sexa-co-ordinate complex with a pseudo-octahedral configuration and at the same time causing a bathochromic shift of the ligand field bands. Hence, if the sexa-co-ordination is not possible for one reason or another, the complex is expected to keep the quadri-co-ordinate, planar configuration, displaying the ligand field band in a frequency region much higher than when the sexa-co-ordination is allowed. An example is bis(*N, N*-diethylethylenediamine)copper(II) perchlorate in the crystalline state, which owes its red color to the steric condition of the ligands. In this case, the steric condition makes it more or less difficult for other ions or molecules to occupy the fifth and sixth positions of co-ordination around the cupric ion, although it does not completely exclude the sexa-co-ordination, so that the complex takes up two water molecules in an aqueous solution. This ligand has no nitrogen atom which is capable of participating in π-bonding with the cupric ion, excepting through hyperconjugation. The pink color of this compound, therefore, is due not to the π-bonding, but to the special steric condition of the ligand.

TABLE IV. MAIN ABSORPTION MAXIMA OF SQUARE-PLANAR COMPLEXES OF COPPER(II), [Cu A_4] OR [Cu B_2]

A or B	ν_{max}	Sample	Ref.
deen	63.4	Crystal	a
Biguanide	61.9	Powder	b
sucim	61.2	Crystal	a
Dicyandiamidine	58.8	Powder	b
Phenylbiguanide	58.4	Powder	b
Biuret	59.4	Crystal	c

ν: 10^{13} sec^{-1}

a) The present measurement

b) M. Kato, Y. Komuro and K. Sone, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **78**, 896 (1957).

c) Quoted in Ref. 13 of the text.

On the contrary, the steric condition does not seem to be the main reason for the formation of the red cupric complexes of succinimide, biuret, biguanide and phenylbiguanide with a square-planar co-ordination. In these cases, there is little steric hindrance which might prevent other ligands from coming closer to the cupric ion in the direction perpendicular to the $Cu(N)_4$-plane. It is readily found that these ligands all involve a similar kind of linkage around the nitrogen atom, which is capable of entering into π-bonding with the cupric ion. It is likely that, in the cupric complexes of this sort, the π-bonding plays a part in leaving the fifth and sixth co-ordination sites unoccupied. It seems that π-bonding of this sort decreases the effective charge on the cupric ion, weakening the possible copper(II)-to-oxygen bond, which is probably strongly ionic.

The Crystal Absorption Spectra of Bis(succinimidato)bis(alkylamine) copper (II) Complexes.—The compounds with a composition of Cu·(*sucim*)$_2$(amine)$_2$, the amine being methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl or *n*-amyl amine as well as ammonia, are all red in the crystalline state. In order to examine the origin of the unusual color of these compounds, one of the compounds has been chosen. Thus, the dichroism of Cu(*sucim*)$_2$(isopropylamine)$_2$ has been determined by the microscopic method; the results of the measurements are shown in Fig. 5 and in Table V.

The succinimidate ion can be combined with the cupric ion through either the nitrogen or the oxygen atom. The co-ordination in this compound, however, is most probably through

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[15] See, for example, C. K. Jørgensen, Proceedings of Tenth Solvay Conference, Brussels, May, 1956.

[16] S. Yamada and R. Tsuchida, This Bulletin, **29**, 289 (1956).

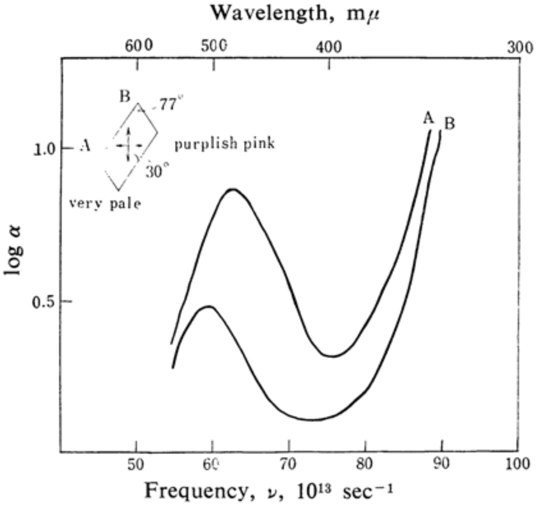

Fig. 5. Polarized absorption spectra of [Cu·(*sucim*)$_2$(*iso*-$C_3H_7NH_2$)$_2$].

TABLE V. ABSORPTION MAXIMA OF [Cu·(*sucim*)$_2$(*iso*-$C_3H_7NH_2$)$_2$] IN THE CRYSTALLINE STATE

	ν_{max}	log α	Half width	Assignment	K
A-abs.	62.6	1.38	12.0	ν_1, ν_2	54.5×10^3
B-abs.	59.1	0.99	11	ν_1	22.2×10^3

ν : 10^{13} sec^{-1}

In the calculation of K, the value of 1.38 was used for the density of the crystal, which was determined with a picnometer. $K=10\alpha M/\rho$ where M and ρ denote molecular weight and density, respectively.

the nitrogen atom, and not through the oxygen atom, as has been discussed in the earlier part of the present paper. There is very little doubt that the amine molecules, besides the unidentate succinimidate ions, are linked with the cupric ion.

The present measurement indicates that the red crystal of Cu(*sucim*)$_2$(*iso*-$C_3H_7NH_2$)$_2$ shows a ligand field absorption band, with its maximum at about 61×10^{13} sec^{-1}, in addition to a strong absorption in the far higher frequency. The absorption maximum of the ligand field band of this compound lies at a much higher frequency than that of most cupric complexes with nitrogen-co-ordinating ligands of an ordinary type, such as ammonia, ethylenediamine and related compounds. This fact shows that there is an essential difference in configuration between Cu(*sucim*)$_2$(*iso*-$C_3H_7NH_2$)$_2$ and [Cu en$_2$ (OH$_2$)$_2$] (NO$_3$)$_2$, since *sucim* stands much lower in the spectrochemical series than en, *deen* or ammonia. It was formerly assumed that an absorption maximum of the ligand field band is displaced bathochromically, when a square-planar complex of copper(II) takes up two more ligands to form a sexa-co-ordinate, pseudo-octahedral complex[11,12,15]. It is, therefore, concluded that Cu(*sucim*)$_2$(amine)$_2$ in the crystalline state consists of quadri-co-ordinate, planar cupric complexes, with the two co-ordination sites, perpendicular to the complex-plane, kept unoccupied. It has not been determined in the present study whether the complex belongs to a cis- or a trans-series.

Since the crystal structure analysis is not available and usually the complex-planes are not all parallel to each other, it is not possible to determine exactly the component absorption coefficients of the planar complex. From the empirical rules, however, one can readily find the main characteristics of the z- and xy-absorptions by using the polarization measurements, which are shown in Table V along with a tentative assignment of the absorption bands. It is found, from the intensity of the ligand field band, that the A- and B-absorptions represent the main features of the xy- and z-absorptions of the complex respectively. For Cu(*sucim*)$_2$(*iso*-$C_3H_7NH_2$)$_2$, the z-absorption shows one component band at about 59×10^{13} sec^{-1}, whereas the xy-absorption, having a much larger oscillator strength than the z-absorption, is assumed to represent the superposition of two component absorption bands, with the main maximum at about 62.7×10^{13} sec^{-1}. The observed polarization property of the absorption bands of this complex is quite similar to that of the other cupric complexes with a square-planar configuration, such as [Cu(*sucim*)$_4$]$^{2-}$ and [Cu(*deen*)$_2$]$^{2+}$, and agrees with the theoretical prediction. Strictly speaking, the symmetry of the complex, Cu·(*sucim*)$_2$(*iso*-$C_3H_7NH_2$)$_2$, deviates from D_{4h}, but it is assumed that the spectrum may be treated approximately in the scheme of D_{4h} field symmetry.

The corresponding compounds of the bis-(succinimidato)-copper(II) complexes with other amines are colored quite similarly to Cu(*sucim*)$_2$(*iso*-$C_3H_7NH_2$)$_2$. Although they are rather unstable in the atmosphere and undergo slow decomposition during the prolonged dichroism measurements, it was possible to determine, by quick measurements, the approximate band maxima of the compounds (about 60×10^{13} sec^{-1}); these lie in the neighborhood of the ligand field band of the corresponding compound with isopropyl amine, but they are at a much higher frequency than the maximum of [Cu en$_2$(OH$_2$)$_2$] (NO$_3$)$_2$. It is concluded that all these homologues consist of quadri-co-ordinate, square-planar complexes, with the fifth and sixth site kept empty. With ethyl amine, the compound has two water molecules of crystallization, but these water molecules are presumed to have nothing to do with the linkage to the copper(II) ion.

There are violet complexes, in addition to the red ones, for ammonia and methyl amine. The examination of the violet form is now progress, and the results will be reported on elsewhere.

The Structure of Bis(succinimidato)bis(alkylamine)copper(II) in Solvents.—The red crystals of Cu(*sucim*)$_2$(amine)$_2$, in general, are unstable in water, ethanol and pyridine. In water, they apparently undergo decomposition and form a pale-blue precipitate upon standing in this solvent for a sufficiently long time. In ethanol and pyridine, the decomposition was not so fast as in water, but the replacement of one of the ligands by a molecule of the solvent seems to take place, along with the addition of the solvent molecules to the cupric complex. On the contrary, the red crystals of the compounds are dissolved in chloroform to form a stable solution with a dark-blue color, which is quite different from the color of the compound in the crystalline states.

The absorption spectra of these compounds in chloroform have been determined in the present work. As may be seen in Fig. 6 and Table VI, the compounds with a formula of Cu(*sucim*)$_2$(amine)$_2$ in chloroform exhibit, in the visible region, one ligand field band with a maximum at about 48 to 50×10^{13} sec^{-1} (625 to 600 mμ), which is far lower than the frequency of the absorption band of the same compounds in the crystalline state. The shift of the band on going from the crystal to the solution is found to be about 11×10^{13} sec^{-1} for the *n*-alkyl amines and about 13×10^{13} sec^{-1} for the isopropyl amine. The shift observed in the present study is much larger than would be expected for typical solvent effects upon the ligand field band with no change in the configuration of the complex. It seems to be evident that, when the crystals are brought into chloroform, some remarkable change in the configuration occurs to the complex-molecules existing in the crystals, in which the complex-molecules have a square-planar co-ordination of the four nitrogen atoms around the cupric ion.

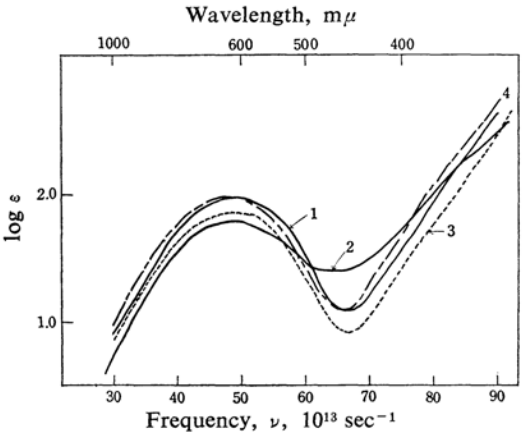

Fig. 6. UV-absorption spectra of [Cu(*sucim*)$_2$·(R·NH$_2$)$_2$] in chloroform 1, R=C_2H_5; 2, R=CH_3; 3, R=*n*-C_3H_7; 4, R=*iso*-C_3H_7

The dissociation of one of the four ligands is quite unlikely, since Beer's law is generally obeyed in the concentration range examined. The present study also reveals that no decomposition of the complexes takes place; at least none takes place at a concentration between 4×10^{-3} and 2×10^{-4} M. The replacement of one of the amine molecules seems to be improbable, since, though chloroform might be bound to a metallic ion, it could only be so very weakly, and since the linkage between the cupric ion and chloroform, if formed at all, would be far weaker than the linkage between the cupric ion and the amine or succinimidate.

It might also be assumed that the chloroform molecules would be co-ordinated, though very weakly, with the cupric ion slightly farther in the direction perpendicular to the complex-plane formed by the cupric ion and the four nitrogen atoms. Judging from the weak perturbing power of the chloroform molecule, this assumption does not seem to explain the enormously large shift of the band maximum on going from the crystal to the solution.

TABLE VI. ABSORPTION MAXIMA OF [Cu(*sucim*)$_2$(R·NH$_2$)$_2$] IN NON-CO-ORDINATING SOLVENTS

R	in $CHCl_3$		in CH_2Cl_2		in C_6H_6	
	ν_{max}(log ε)	h. w.	ν_{max}(log ε)	h. w.	ν_{max}(log ε)	h. w.
CH_3	49.6 (1.79)	21.8	50.4 (1.90)	18.7	insoluble	
C_2H_5	49.4 (1.98)	18.7	49.6 (1.85)	19.2	47.1 (1.71)	18.3
n-C_3H_7	48.9 (1.86)	19.0	50.0 (1.98)	18.6	48.3 (1.86)	18.8
iso-C_3H_7	48.6 (1.97)	18.9	49.8 (1.96)	18.9	48.8 (1.93)	18.8
n-C_4H_9	49.2 (2.02)	18.8	50.2 (1.97)	18.8	48.4 (1.96)	18.2

ν: 10^{13} sec^{-1} h. w.: half width in 10^{13} sec^{-1}

It is expected theoretically, and has been confirmed experimentally, that the ligand field band of a cupric complex suffers a more or less bathochromic shift when the square-planar complex takes up ligands to form an octahedral complex. However, the chloroform molecule usually has so slight an ability to be bound to the metallic ion that the band shift on going from the square-planar complex to the chloroform adduct with a pseudo-octahedral configuration would be much smaller than the corresponding effects of water as well as of ammonia molecules. On the contrary, the present measurements show that the difference in the band maximum between the crystal and the chloroform solution is usually great, the ratio of the maximum frequency of the crystal to that of the chloroform solution deviating remarkably from unity. The values ranging from 0.70 to 0.80 for the succinimidato-complex in chloroform are much smaller even than the values expected for the effects of ammonia molecules as the additional ligands as well as for those of water molecules. It is to be recalled that the corresponding ratio of the crystal to the aqueous solution is about 0.80 in the case of the bis(diethylethylenediamine) complex. The observed ratio for the chloroform solution seems to be too small for the octahedral model with the chloroform molecules in trans-positions.

It may be assumed that the ligand field around the cupric ion of the succinimidato complex is determined mainly by the four nitrogen atoms and is affected only very little by such other ligands, like chloroform molecules, as might occupy the remaining co-ordination sites in the compound. In the light of the discussion above, therefore, the enormous band shift on going from the crystal to the chloroform solution indicates that the co-ordination of the four nitrogen atoms around the cupric ion within the Cu(*sucim*)$_2$(amine)$_2$ complexes in chloroform deviates from a square-planar configuration. In this connection, it is to be noted that the ligand field bands of all these compounds in non-co-ordinating solvents have a much higher intensity and a larger half-width than most cupric complexes with a tetragonal field symmetry. This is in agreement with the theory which predicts that a complex of a transition element with no center of inversion will show a ligand field band of a higher intensity than a complex with a center of inversion. According to the crystal field theory, however, the regularly tetrahedral complex will show a ligand field band in a frequency region much lower than that observed in the present study, since the quadri-co-ordinate complex with a regularly tetrahedral configuration would have a ligand field-splitting parameter which is about 4/9 times that of the octahedral complex. The regular or near regular tetrahedral model seems to be less likely.

One may assume that the oxygen atoms of the carbonyl-groups will be bound to the cupric ion to form a pseudo-octahedral complex. This effect alone, however, is not regarded as strong enough to explain the observed remarkable difference in the absorption maximum between the crystal and the chloroform solution, since the oxygen atom of this type is known to be bound only very weakly to the metal ion. However, even so, this probably plays a part in causing the deviation from the square-plane of the co-ordination in such a way that this weak linkage may help and keep the configuration deviated from the square-plane.

The cupric complexes of the Cu(*sucim*)$_2$-(amine)$_2$ type are also soluble in methylene chloride and benzene to give a stable solution, which is colored dark-blue. As is shown in Fig. 7 and Table VI, the absorption spectra of the compounds in these solvents have main features which are similar to those of the compounds in chloroform. All the compounds show a similar spectrum in these solvents; therefore, the absorption spectra of only some of the compounds are shown in Fig. 7. It is found that bis-(succinimidato)bis(ethylamine)-copper(II) in benzene, for example, shows a ligand field band at a frequency nearly equal to that of the chloroform solution. As in the case of the chloroform solution, it is concluded that the co-ordination of the four nitrogen atoms around the cupric ion with the Cu-(*sucim*)$_2$(amine)$_2$ complex in these solvents

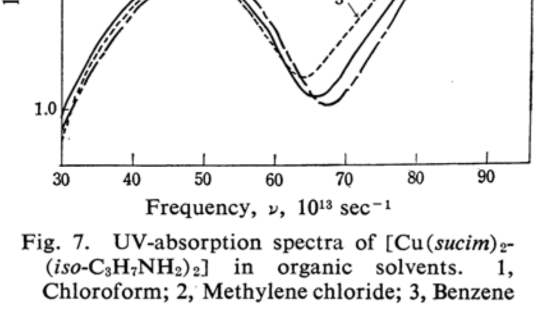

Fig. 7. UV-absorption spectra of [Cu(*sucim*)$_2$-(*iso*-$C_3H_7NH_2$)$_2$] in organic solvents. 1, Chloroform; 2, Methylene chloride; 3, Benzene

probably deviates from the square-planar configuration.

In these non-polar solvents, the oxygen atom of the succinimidate ion of the cupric complex may be subjected to repulsion by the molecules of the solvents, so that the rejected oxygen atom will point toward the cupric ion to form weak linkage with it. When alcohols or water are used as a solvent, however, the oxygen atom in the succinimidate ion is assumed to be associated with the solvent molecule, possibly through hydrogen bonding, since the affinity of this type of the oxygen atom to the cupric ion may be small. Moreover, the molecules of these polar solvents can be co-ordinated to the cupric ion, whereas the molecules of the non-polar solvents, in general, cannot. This probably explains the difference in the configuration of the succinimidato-complexes between the solutions in the polar and in the non-polar solvents. The minor difference in the frequency of the absorption maximum between the solutions in chloroform and the other non-polar solvents is to be ascribed not to the difference in the configuration of the complex in these solvents, but to an ordinary kind of perturbation on the complex by the solvents.

Summary

The dichroism in the visible and ultraviolet region has been determined by the microscopic method with single crystals of $K_2Cu(\textit{sucim})_4 \cdot 6H_2O$, $Cu(\textit{deen})_2(ClO_4)_2$ and $Cu(\textit{sucim})_2(\textit{iso-}C_3H_7NH_2)_2$. From a comparison of these spectra with the spectra of most cupric complexes, it has been concluded that these compounds contain square-planar complexes of copper(II), with the fifth and sixth co-ordination sites left empty. It has been concluded, in a similar way, that the compounds with a formula of $Cu(\textit{sucim})_2(\text{amine})_2$, the amine being methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl and *n*-amyl amines as well as ammonia, consist of quadri-co-ordinate, square-planar complexes in the crystalline state.

The absorption spectra of bis(succinimidato)-bis(alkylamine)-copper(II) complexes in chloroform, benzene and methylene chloride, in which the compounds are colored dark-blue, have been determined. The enormously large band shift toward a lower frequency, on going from the crystal to the solution, seems to indicate that the configuration in these solvents is not the square-planar or trans-bis-(chloroform) configuration, but deviates from the square-plane.

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Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka