December, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(12), 3049—3056 (1974) 3049

Six-coordinate Copper(II) Complexes Derived from the Reactions of Bis(acetylacetonato)- and Bis(ethyl acetoacetato)-copper(II) with Some Bidentate Nitrogen Bases

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(Received July 22, 1974)

Green-to-blue six-coordinate mixed complexes, Cu(acac)$_2$(en) and Cu(etac)$_2$(diamine)(acac=acetylacetonate anion; etac=ethyl acetoacetate anion; diamine=ethylenediamine, trimethylenediamine, 2,2′-bipyridine or 1,10-phenanthroline) have been isolated by the reactions of the respective parent β-diketonate with the corresponding diamine in dry dichloromethane. On the other hand, the reaction of Cu(acac)$_2$ with en in the mole ratio of one-to-two in dichloromethane saturated with water has resulted in purple crystals of Cu(acac)$_2$(en)$_2$·2H$_2$O. This compound has been shown by X-ray analysis to consist of a square-planar copper(II) cation, coordinated by two ethylenediamine molecules, and two planar acetylacetonate anions, the plane of which is not perpendicular to, but slanted against, the CuN$_4$ plane. One oxygen atom of the anion participates in the N–H···O hydrogen bonding with an NH$_2$ group of the ethylenediamine molecule, while the other occupies the axial position of Cu(en)$_2$$^{2+}$ (Cu···O: 2.79(1) Å). Therefore, the compound can be designated by the formula [Cu(en)$_2$]·(acac)$_2$·2H$_2$O. The water hydrogen atoms seem to take part in the hydrogen bonding with the anion oxygen atoms.

It is well-known that the bis(β-diketonato)copper(II) complexes may behave as Lewis acids and react with nitrogen bases to form addition compounds.[1] Several five-coordinate addition compounds of square-planar bis(β-diketonato)copper(II) complexes with heterocyclic nitrogen bases have been isolated.[2–6]

The Lewis acidity of the bis(β-diketonato)copper(II) complexes is affected by the relative electron-withdrawing power of the β-diketonate ligand.[7,8] When, for example, the highly electronegative CF$_3$-group is introduced in plane of the CH$_3$-group in acetylacetone, the affinity of the copper atom for the axial ligand is enhanced and the addition of two molecules of a monodentate nitrogen base proceeds quite readily. Thus, many six-coordinate addition compounds of bis(trifluoroacetylacetonato)-,[6,9] bis(hexafluoroacetylacetonato)-[6–8] and bis(thenoyltrifluoroacetonato)-[6,10] copper(II) complexes with monodentate nitrogen bases have been isolated thus far. Similar 1 : 2 adducts of the monodentate nitrogen base are also produced with the copper(II) complexes in which the central methine proton of the parent acetylacetonate ligand is replaced by another electron-withdrawing substituent, such as a nitro- or cyano-group.[11]

On the other hand, there have been only a few reports concerning the reactions of bis(β-diketonato)copper(II) with bidentate nitrogen bases. A stable 2,2′-bipyridine adduct of bis(hexafluoroacetylacetonato)copper(II) was isolated, as its structure was determined by means of single-crystal X-ray analysis.[12] More recently, another research group has also described the reaction of the same copper(II) complex with some chelating diamines including ethylenediamine.[13,14]

We wish now to report on the reactions of bis(acetylacetonato)copper(II), Cu(acac)$_2$, with ethylenediamine (en), and of bis(ethyl acetoacetato)copper(II), Cu(etac)$_2$, with en, trimethylenediamine (tn), 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen).

Results and Discussion

Six complexes have been isolated; they are listed in Table 1, together with their analytical and magnetic data. All these complexes have normal magnetic moments as monomeric copper(II) compounds.

The 1 : 1 Complex Yielded by the Reaction of Bis(acetylacetonato)copper(II) with Ethylenediamine in Dry Dichloromethane. The reaction of Cu(acac)$_2$ with equimolar en in dry dichloromethane gave a pale green precipitate, composed of the 1 : 1 adduct of the parent complex with en. The same adduct was also obtained by the reaction of the parent complex suspended in dry ether

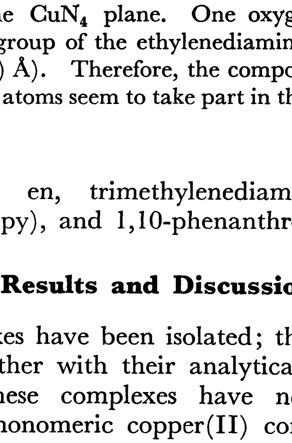

Fig. 1. The diffuse reflectance spectra of: (1), Cu(acac)$_2$; (1a), Cu(acac)$_2$(en); (2), Cu(etac)$_2$; (2a), Cu(etac)$_2$(en); (2b), Cu(etac)$_2$(tn); (2c), Cu(etac)$_2$(bipy); (2d), Cu(etac)$_2$(phen) and (3), [Cu(en)$_2$](acac)$_2$·2H$_2$O.

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TABLE 1. COLOR, CHEMICAL ANALYSES, AND MAGNETIC MOMENTS OF THE ISOLATED COMPLEXES

	Color	Found (%)				Calcd (%)				μ_{eff} (B.M.)
		C	H	N	Cu	C	H	N	Cu	
1 : 1 Complexes										
$Cu(acac)_2(en)$	pale green	44.60	6.93	8.78	19.36	44.78	6.89	8.70	19.74	1.84
$Cu(etac)_2(en)$	pale blue	43.07	6.89	7.37	16.83	44.03	6.86	7.33	16.64	1.88
$Cu(etac)_2(tn)$	pale green	45.40	7.32	6.81	15.68	45.50	7.13	7.07	16.05	1.99
$Cu(etac)_2(bipy)$	green	55.60	5.54	5.74	13.32	55.28	5.48	5.86	13.29	1.81
$Cu(etac)_2(phen)$	green	57.25	5.26	5.86	13.16	57.53	5.23	5.59	12.68	1.94
1 : 2 Complex										
$[Cu(en)_2](acac)_2\cdot 2H_2O$	purple	39.50	8.12	13.27	15.09	40.23	8.20	13.40	15.20	1.84

TABLE 2. FREQUENCIES (kK) OF MAXIMUM ABSORPTIONS IN DIFFUSE REFLECTANCE SPECTRA

Parent complexes				
$Cu(acac)_2$			15.0	18.0
$Cu(etac)_2$			14.9	17.3
1 : 1 Complexes				
$Cu(acac)_2(en)$	8.7	13.6	14.6	
$Cu(etac)_2(en)$	—	12.8	15.4	
$Cu(etac)_2(tn)$	—	12.8	15.6	
$Cu(etac)_2(bipy)$	—	13.4	14.9	
$Cu(etac)_2(phen)$	—	11.9	14.4	
1 : 2 Complex				
$[Cu(en)_2](acac)_2\cdot 2H_2O$		—	—	18.9

TABLE 3. CHARACTERISTIC IR BANDS OF THE DIAMINE GROUP IN BIS(ACETYLACETONATO)ETHYLENEDIAMINECOPPER(II) AND THE CORRESPONDING ETHYLENEDIAMINE-d_4 COMPLEX

$Cu(acac)_2(en)$	$Cu(acac)_2$-(en-d_4)	ν_{NH_2}/ν_{ND_2}	Assignment
3240 m	2400 w	1.35	NH_2 stretch
3160 m	2335 w	1.35	
~1600[a)]	1183 w	1.35	NH_2 scissor
1332 m	1005 m	1.33	NH_2 wag
1159 m	900 m	1.29	
1110 w, sh	885 sh	1.25	NH_2 twist
1021 m	750 w	1.36	
785 m			NH_2 rock

a) This band is obscured by the intense absorption of the acetylacetonate ligand.

with en. The product can hardly be dissolved in usual organic solvents at room temperature without partial dissociation. However, it can be recrystallized from hot benzene. It is decomposed in moist air and turns violet, but it is stable for a long time under dry conditions.

The ligand-field spectrum of $Cu(acac)_2$ shows two indefinite absorption maxima at about 15.0 and 18.0 kK,[1)] while that of the mono-pyridine adduct has only one broad absorption maximum at 15.2 kK.[15–17)] On the other hand, the diffuse reflectance spectrum of the present 1 : 1 adduct of $Cu(acac)_2$ with en has two definite absorption maxima, one appearing at 14.6 kK, accompanied by an indefinite shoulder at about 13.6 kK, and the other, at 8.7 kK (Fig. 1, 1a and Table 2). These spectral features fit in well with the step-by-step change in the stereochemistry around the copper atom from square-planar $Cu(acac)_2$ through the five-coordinate pyridine adduct to the tetragonally-distorted octahedral environment, as was shown for the bis(acetylacetonato)- or bis(hexafluoroacetylacetonato)-copper(II)-pyridine system by Funch and Ortolano.[7)] Recently, very similar spectra have been reported for the bis(pyridine) adducts of the copper(II) γ-nitro- and γ-cyano-acetylacetonates.[11)]

The IR spectra of the 1 : 1 adduct of $Cu(acac)_2$ with en in the higher-frequency region, except for 1700—1500 cm^{-1}, can be understood, on the whole, as an overlap of the spectra of the acetylacetonate ligand and coordinated en. By a recent isotopic study[18,19)] of the IR spectra of $Cu(acac)_2$, two absorption bands in the carbonyl region were definitely assigned: the band at 1578 cm^{-1} mainly to the C=O stretching vibration, and the second one, at 1527 cm^{-1}, to the antisymmetric vibration of the C—C—C segment of the chelate ring. On the other hand, in the IR spectra of the en adduct, the band assignable to the carbonyl stretching is shifted to the higher-frequency side (1615 cm^{-1}), while the other is shifted to the lower-frequency side (1501 cm^{-1}). These shifts may be caused by a weakening of the copper-ligand bond due to the coordination of diamine. Similar spectral features have also been observed for $Mn(acac)_2(en)$.[20)] Characteristic bands attributable to the diamine ligand are listed in Table 3; they were assigned by reference to the literature[21)] and also to the deuteration effect. There are no bands due to free diamine in the frequency region higher than 3320 cm^{-1}, indicating that both nitrogen atoms of the diamine are linked to the copper atom.

Figure 2 shows the far-IR spectra of the complex, together with those of $Cu(acac)_2$ and $Cu(etac)_2$ as references. The spectra of $Cu(acac)_2$ (1) have three bands between 600 and 280 cm^{-1}, two of which (455 and 291 cm^{-1}) are assigned to the pure Cu–O stretching modes.[22)] In the case of the 1 : 1 en adduct (1a), the band near 450 cm^{-1} disappeared, while three intense bands (572, 545 and 490 cm^{-1}) and one broad band (415 cm^{-1}) appeared. The former bands are assigned to the ring vibrations of the en chelate ring, while the latter is assumed by reference to the literature[23)] to be an overlap of the Cu–O (415 cm^{-1}) and the Cu–N (405 cm^{-1}, shoulder) stretching vibrations.

It is obvious from the analytical and spectroscopic results presented above that the 1 : 1 en adduct with

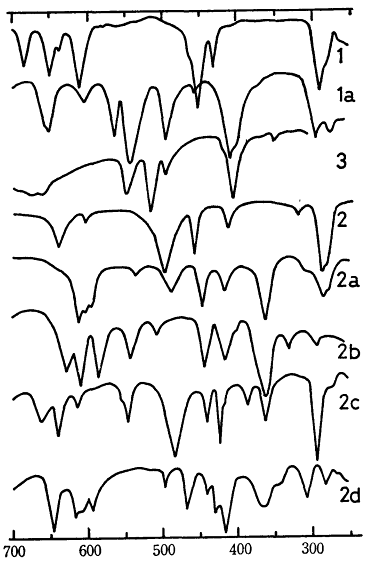

Fig. 2. The far-IR spectra of: (1), Cu(acac)$_2$; (1a), Cu(acac)$_2$(en); (2), Cu(etac)$_2$; (2a), Cu(etac)$_2$(en); (2b), Cu(etac)$_2$(tn); (2c), Cu(etac)$_2$(bypy); (2d), Cu(etac)$_2$(phen) and (3), [Cu(en)$_2$](acac)$_2$·2H$_2$O.

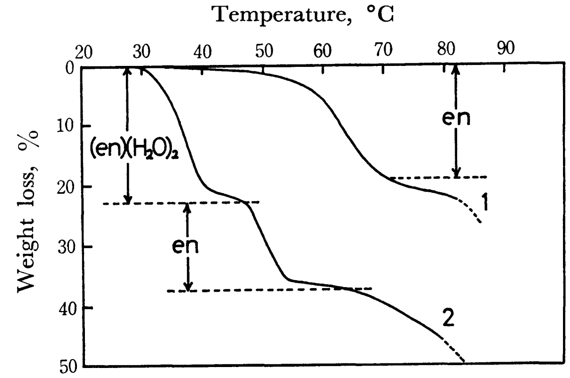

Fig. 3. The thermogravimetric curves of: (1), Cu(acac)$_2$(en) and (2), [Cu(en)$_2$](acac)$_2$·2H$_2$O.

Cu(acac)$_2$ is the first example of an isolated stable adduct which has an octahedral stereochemistry around the copper atom, without any electron-withdrawing substituent in the acetylacetonate ligand. This stability may be attributed to the chelating effect of the diamine ligand. However, its thermal stability is not so high as that of the corresponding manganese complex,$^{20)}$ which begins to decompose at around 95 °C. The thermogravimetric analysis, as is shown in Fig. 3 (1), indicates that Cu(acac)$_2$(en) begins to decompose at around 35 °C, thus liberating en, which was identified by a method described previously.$^{20)}$ The weight loss below 72 °C amounts to 19% just fitting the calculated value of 18.7% for the en content in this adduct. When a sample was heated further, a rapid weight loss occurred because of the sublimation of the residual bis-chelate.

Martell and Calvin$^{24)}$ pointed out that the formation of a quadridentate imine from acacH and en is catalyzed by Cu(II) ions in aqueous solutions. Candlin, Taylor and Thompson$^{25)}$ also assumed that the reaction probably involves the attack of en on the coordinated acetylacetone. However, our results have revealed that such a reaction does not occur, at least not in dichloromethane at room temperature. It might occur at higher temperatures, although attempts to cause the primary amine adducts of bis(β-diketonato)nickel(II) to undergo a Schiff-base rearrangement in nonpolar solvents were unsuccessful,$^{26)}$ as was an attempt to prepare an imine from the bis(haxafluoroacetylacetonato)ethylenediaminecopper(II) complex by a gas-phase template reaction.$^{13c)}$

The 1 : 1 Complexes Yielded by the Reactions of Bis(ethyl acetoacetato)copper(II) with Some Diamines in Dichloromethane. Only the en adduct was isolated in several attempts to prepare diamine adducts with Cu(acac)$_2$. On the contrary, the reactions of Cu(etac)$_2$ with en, tn, bipy, and phen gave the corresponding 1 : 1 diamine adducts. This may be due to the Lewis acidity of the parent complex, enhanced by the substitution of the ethoxy group into the acetylacetonate ligand.$^{3)}$ All these complexes were isolated as green-to-blue crystals. They are stable in air relative to Cu(acac)$_2$(en), but are unstable in solution and partially dissociate into Cu(etac)$_2$ and the diamine.

The diffuse reflectance spectra of these adducts (Fig. 1, 2a-2d and Table 2) exhibit shifts similar to those observed for Cu(acac)$_2$(en), but a new maximum does not appear around 8 kK. Thus, a question is raised whether or not these complexes have an octahedral stereochemistry around the copper atom. However, the maximum absorptions of these spectra differ clearly from those of five-coordinate pyridine or the substituted pyridine adducts of Cu(etac)$_2$, in which only one broad absorption maximum is observed, at 14.1 kK.$^{3,16)}$ Moreover, a discrepancy similar to the one mentioned above in the reflectance spectra is also observed between the two spectra of dihydrate and the bis(pyridine) adduct of copper(II) hexafluoroacetylacetonate.$^{7)}$ There is no doubt, in light of the spectral similarity with diamine adducts of copper(II) hexafluoroacetylacetonate and the IR spectral evidence to be presented in the next paragraph, that these complexes have a six-coordinate octahedral stereochemistry around the copper atom.

The IR spectra of parent complexes in the higher-frequency region are also composed of those due to the ethyl acetoacetate ligand and those due to the coordinated diamine. However, a significant and diagnostic difference caused by the coordination of a diamine is observed in the ν(C=O) region. These spectra exhibit two or three medium-to-strong bands between 1700 and 1500 cm^{-1}: (a) Cu(etac)$_2$(en), 1653(s), 1615(m), 1517(s) cm^{-1}; (b) Cu(etac)$_2$(tn), 1652(s), 1610 (m), 1521(s) cm^{-1}; (c) Cu(etac)$_2$(bipy), 1660(s), 1613 (s), 1517(s) cm^{-1}; (d) Cu(etac)$_2$(phen), 1646(s), 1514 (s) cm^{-1}. Of those listed above, one medium band of each aliphatic diamine adduct was assigned to the NH$_2$ deformation mode on the basis of the deuteration effect, while the strong band at 1613 cm^{-1} of the bipy adduct was assigned to the bipy-ring vibration.$^{27)}$ The remaining two bands on each adduct around 1650 and 1515 cm^{-1} were assigned mainly to the C=O stretching vibration and the antisymmetric vibration of the C-

C–C segment of the chelate ring, by reference to the assignment of the acetylacetonate complex. The higher-frequency shift of the former band and the lower-frequency shift of the latter band from those (1600 and 1536 cm^{-1}) in the parent complex, Cu(etac)$_2$, are both larger than the corresponding shifts in the case of Cu(acac)$_2$(en). This may suggest that the weakening of the copper-ligand bond strength by the coordination of diamine is larger than in the case of Cu(acac)$_2$(en). Relevant shifts were also noticed in the region of ester absorption bands: that is, the "ester C–O–R bands" (1291(s) and 1184(s) cm^{-1}) of the parent Cu(etac)$_2$ shift to 1237(s), 1173(s) (en complex), 1234(s), 1173(s), (tn complex), 1277(s), 1117(s) (bipy complex), and 1226(s), 1165(s) (phen complex) cm^{-1} respectively. Such large shifts of the "ester C–O–R" bands to the lower-frequency side are accompanied by a shift of the carbonyl C=O band to the higher-frequency side, disclosing a significant weakening of the "ester carbonyl" (C=O)-copper bond strength in comparison with that of the parent Cu(etac)$_2$.

The spectra of both en and tn adducts exhibit characteristic bands due to the diamine ligand at 3320, 3260, and 3160 cm^{-1} and at 3320(sh), 3270, and 3160 cm^{-1} respectively. They also have no bands due to free diamine in the frequency region higher than 3320 cm^{-1}. This may indicate coordination by both nitrogen atoms of the diamines. The coordination of phen to the copper atom is evidenced by the splitting of the strong bands at 728 and 850 cm^{-1}.[27] In the spectra of the bipy adduct, the shift and split of the characteristic band (751 cm^{-1}) of the free bipy ligand to 777 and 785 cm^{-1} may also reveal the complexation of bipy to the copper atom.[27,28]

The far-IR spectra of Cu(etac)$_2$ and its 1 : 1 diamine adducts are shown in Fig. 2(2, 2a—2d). The band at 454 cm^{-1} assignable to the ν(Cu–O) in the spectra of parent complex (2) will be shifted to the lower-frequency side by the addition of diamine. Hence, for adducts containing aliphatic diamine the bands at 446 cm^{-1} (en complex, 2a) and 443 cm^{-1} (tn complex, 2b) were assigned to the ν(Cu–O) vibrations, and the new strong bands at 363 cm^{-1} (en complex, 2a) and 360 cm^{-1} (tn complex, 2b), to the ν(Cu–N) vibrations. In the case of adducts containing heterocyclic diamine, their spectra are more complicated because of their many ligand vibrations. The ν(Cu–O) bands of the bipy and phen adducts (2c and 2d) can not be unequivocally assigned, although they are expected to appear in the 400—450 cm^{-1} region. The bands at 296 cm^{-1} (bipy complex, 2c) and 279 cm^{-1} (phen complex, 2d) were also assigned to the ν(Cu–N) vibrations, according to the literature.[29]

From all the above discussion, it may be concluded, with regard to the structure of the 1 : 1 diamine adducts, that the apical positions are occupied by the two carbonyl oxygen (or ester carbonyl oxygen) atoms of the four originally-coordinating oxygen atoms of planar chelate, and that the equatorial plane is composed of the residual two oxygen atoms and two nitrogen atoms of the diamine ligand, as is shown in Fig. 4. Such a structure has also been proposed for Cu(etac)$_2$ in pyridine.[30]

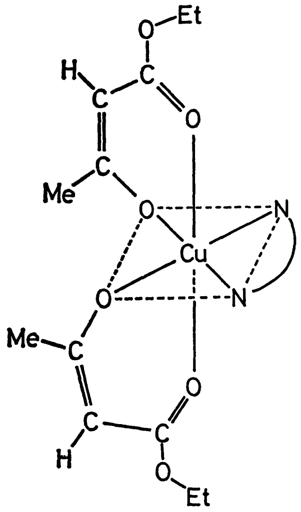

Fig. 4. The suggested structure of Cu(etac)$_2$(diamine).

Graddon and Watton[3] isolated the bis(pyridine) adduct of Cu(etac)$_2$, but concluded that the second molecule of pyridine was only filling spaces in the crystal lattice and was not coordinated to the copper atom. Therefore, the 1 : 1 diamine adducts of Cu(etac)$_2$ isolated here seem to be the first examples of stable adducts with an octahedral stereochemistry around the copper atom.

The 1 : 2 Complex Yielded by the Reaction of Bis(acetylacetonato)copper(II) with Ethylenediamine in Wet Dichloromethane.[31] The reaction of Cu(acac)$_2$ with en in the mole ratio of one-to-two in wet dichloromethane gave a violet precipitate composed of two en molecules, two acetylacetonate anions, and two water molecules per copper atom. It dissolves in water to give a violet solution, and in methanol to result in a blue solution with some decomposition, but it is insoluble in non-polar organic solvents.

The diffuse reflectance spectrum of the compound is entirely different from that of Cu(acac)$_2$ (Fig. 1 (3) and Table 2). With only one absorption maximum at 18.9 kK, it can be compared with the spectra of the oxyanion salts of the square-planar cations Cu(en)$_2^{2+}$; for the sulphate, nitrate, and perchlorate, the maxima are observed at 17.6, 18.6, and 18.8 kK respectively.[32] The shifts to a higher frequency are attributed to the reduced interaction of the copper atom with the oxygen atoms of the acetylacetonate ligand. This compound may be compared with bis(ethylenediamine)copper(II) perchlorate as to its copper-oxygen bonding character, which may be ionic rather than covalent.

The IR spectrum of the compound differs little from that of Cu(acac)$_2$(en) except for the additional bands due to the lattice water. It has a broad band assignable to the ν(C=O) vibration at 1607 cm^{-1}, and also a strong band assignable to the antisymmetric vibration of the C–C–C segment of the acetylacetonate ligand at 1508 cm^{-1}. It also has bands due to the coordinated diamine at 3200 (shoulder) and 3100 cm^{-1}. As was pointed out by George and Robinson,[33] the bands at 1206 and 768 cm^{-1} in the anhydrous sodium acetylacetonate are split, but they are not split in the dihydrate. These bands are assigned to the C–H in-plane and out-of-plane deformations; their splitting suggests that some interactions occur between adjacent ions in the lattice. However, in our compound, only the former band is split. Even if two moles of en are forced to react with one mole of $Cu(acac)_2$ in dry dichloromethane, only the 1 : 1 complex is formed. Water molecules seem to play a very important role in changing the linkage mode of acetylacetonate ligands.

The far-IR spectra of the compound, as is shown in Fig. 2(3), are very simple, and the sharp band at 403 cm^{-1} is easily assigned to the ν(Cu–N) vibration by comparison with those of $Cu(acac)_2(en)$. As is to be expected from the diffuse reflectance spectrum of the compound, no bands due to the ν(Cu–O) vibration appeared in the frequency region measured. This also suggests that the compound has a square-planar cation, $Cu(en)_2{}^{2+}$, and two acetylacetonate anions.

It seemes interesting to examine the thermal property of the compound because of the anionic character of the acetylacetonate group. As is shown in Fig. 3(2), it decomposed rapidly at temperatures above 30 °C and lost one en and two water molecules below 47 °C, where the curve has a slightly gentle slope. When the temperature of the sample was further raised, the thermogravimetric curve showed the same pattern as that of the 1 : 1 adduct. All this behavior in the thermogravimetric analysis may be represented by the following equation;

$$[Cu(en)_2](acac)_2\cdot 2H_2O \rightarrow Cu(acac)_2(en) \rightarrow Cu(acac)_2$$

It is interesting that the acetylacetonate anions recombine with the copper atom, forming chelate rings by displacing en molecules.

The conductivity of this compound in a 10^{-3} M aqueous solution is 170 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$. This value falls between those of 1 : 1- and 1 : 2-electrolytes, suggesting the occurrence of a dissociation such as the following;

$$[Cu(en)_2](acac)_2\cdot 2H_2O \rightleftarrows [Cu(en)_2]^{2+} + 2acac^- + 2H_2O$$

This dissociation is also evidenced by the visible spectrum of the compound in an aqueous solution.

To ascertain the bonding nature of the acetylacetonate anions and the role of water molecules in this compound, a single crystal X-ray analysis was performed.

A perspective drawing of the complex is shown in Fig. 5. The copper atom lies on a crystallographic center of symmetry and has a square-planar coordination by four N atoms of the two en molecules, which are in a *gauche* conformation. The mean Cu–N bond length is 2.00 Å; this value is comparable with those found in $[Cu(en)_2](BF_4)_2$ (2.02 Å),[34] $[Cu(en)_2](NO_3)_2$ (2.03 Å),[35] and $[Cu(en)_2](NCS)(ClO_4)$ (2.02 Å).[36] The bond lengths and angles are summarized in Table 4.

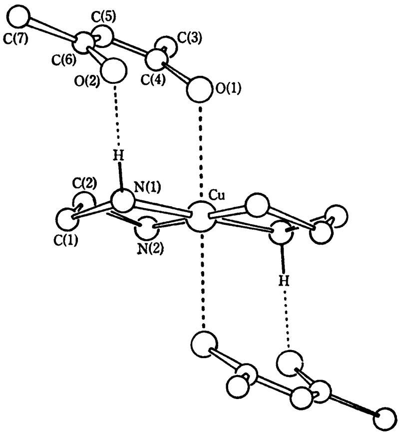

Fig. 5. The structure of $[Cu(en)_2)](acac)_2$.

TABLE 4. BOND DISTANCES AND ANGLES

Cu-N(1)	1.98(1) Å	N(1)-Cu-N(2)	85.9(4)°
Cu-N(2)	2.01(1)	N(1)-Cu-O(1)	82.2(3)
Cu-O(1)	2.79(1)	N(2)-Cu-O(1)	91.1(3)
N(1)-C(1)	1.51(2)	Cu-N(1)-C(1)	109.6(7)
N(2)-C(2)	1.49(2)	Cu-N(2)-C(2)	108.5(7)
C(1)-C(2)	1.51(2)	N(1)-C(1)-C(2)	108.4(9)
O(1)-C(4)	1.23(1)	N(2)-C(2)-C(1)	108.4(9)
O(2)-C(6)	1.26(1)	Cu-O(1)-C(4)	125.7(7)
C(4)-C(5)	1.39(2)	O(1)-C(4)-C(5)	125(1)
C(5)-C(6)	1.38(2)	O(1)-C(4)-C(3)	117(1)
C(3)-C(4)	1.50(2)	C(3)-C(4)-C(5)	118(1)
C(6)-C(7)	1.55(2)	C(4)-C(5)-C(6)	127(1)
		C(5)-C(6)-C(7)	118(1)
		C(7)-C(6)-O(2)	115(1)
		C(5)-C(6)-O(2)	126(1)

TABLE 5. LEAST-SQUARES PLANES IN TERMS OF ORTHOGONAL AXES,* AND DEVIATIONS (Å) OF RELEVANT ATOMS FROM THE PLANES IN SQUARE BRACKETS

Plane of acetylacetonate anion
$-0.501X-0.176Y-0.848Z=-2.31$
[O(1), 0.02; O(2), −0.00; C(3), −0.01; C(4), 0.01; C(5), −0.02; C(6), −0.02; C(7), 0.03 Å]

Plane defined by Cu, N(1) and N(2)
$0.641X+0.598Y+0.481Z=0$
[C(1), −0.28; C(2), 0.36 Å]

* $X=ax+by\cos\gamma+cz\cos\beta$, $Y=by\sin\gamma-cz\sin\beta\cos\alpha^*$ $Z=z/c^*$

The acetylacetonate anion is planar; the equation of the plane is given in Table 5. Moreover, the anion has an approximate mirror plane which is perpendicular to the plane of the anion and which bisects the C(4)—C(5)—C(6) bond angle. Although this suggests a complete delocalization of π electrons in the anion, the accuracy of the bond length and angle is not great enough to allow a definite conclusion to be reached.

The hexacoordinate copper(II) compounds are well-known to show Jahn-Teller distortions. Thus, the four Cu–O bonds in the equatorial plane of the tris(hexafluoroacetylacetonato)cuprate(II), $Cu(hfac)_3{}^-$, average 2.015(5) Å, and the two axial bonds 2.176(7) Å.[37] The mixed complexes, $Cu(hfac)_2(py)_2$[38] and $Cu(hfac)_2$-

(bipy),[12] show the *cis* octahedral CuO_4N_2, and the Cu–O distances *trans* to the Cu–N bonds in the equatorial plane are 1.998(4) Å for the pyridine complex and 1.967(4) Å for the bipy complex, while the axial Cu–O distances are 2.283(6) and 2.296(4) Å respectively.

In the present complex, the Cu–O distances are much more longer than the Jahn-Teller elongation. Of the two oxygen atoms in the acetylacetonate anion, O(1) occupies the axial position of $[Cu(en)_2]^{2+}$ and the Cu···O distance is 2.79 Å. This value is comparable with that (2.793 Å) found in bis(hexafluoroacetylacetonato)bis(*N*,*N*-dimethylethylenediamine)copper(II), $Cu(hfac)_2(dmed)_2$,[13b] indicating that there exists only a weak interaction between Cu and O(1). In $[Cu(en_2](acac)_2\cdot 2H_2O$, the tetragonality ratio, $T = R_S/R_L$, defined by Hathaway,[39] where R_S and R_L are the mean equatorial and axial bond lengths, is 0.68.[40] This value is close to those for the Cu(II) complexes with the square-planar structure[41]; hence, the Cu–O(1) bond can be regarded as essentially ionic in character.

On the other hand, O(2) is close to N(1) (O···N, 3.02 Å), the axial N(1)–H bond protruding towards O(2) with the N(1)–H···O(2) angle of 175°. The interatomic distance between the H and O atoms is estimated to be 2.06 Å, which is considerably smaller than the sum of the Van der Waals radii of these atoms. Thus, N–H···O hydrogen bonding seems to exist between N(1) and O(2), though the direction of the N(1)···O(2) bond is nearly perpendicular to the plane of the anion.

The mode of interaction between the cation and the anion in the present complex is similar to that in $Cu(hfac)_2(dmed)_2$,[13b] but the structure of the former is different from that of the latter. In the hfac analogue, the plane of hfac is almost perpendicular to the plane defined by Cu and four N atoms (interplanar angle, 90.7°), while the Cu···O–C angle is 166.7°. In the present complex, however, the plane of the anion is not perpendicular to the CuN_4 plane, but is, rather, slanted against it (interplanar angle, 34°), with the Cu···O–C angle of 126°; the relative orientation of the cation and the anion is much less favorable to the formation of a covalent Cu–O bond.

The crystal structure viewed down the *b* axis is shown in Fig. 6. There are O–H···O and N–H···O hydrogen bonds in the crystal; they are indicated by dashed lines in the figure. Although no hydrogen atom could be found in the final difference synthesis, these hydrogen bonds were confirmed by deducing the positions of hydrogen atoms.[42] The data of the hydrogen bonds are summarized in Table 6. All the hydrogen atoms in NH_2 groups participate in the N–H···O hydrogen bonding. The oxygen atom of a water molecule is surrounded tetrahedrally by O(1) (1–*x*, 1–*y*, 1–*z*), O(2) (*x*, *y*, *z*), N(1) (–*x*, –*y*, 1–*z*), and N(2) (–*x*, –*y*, –*z*) at distances of 2.79, 2.83, 2.97, and 3.04 Å respectively; hence, both of the water H atoms seem to take part in hydrogen bonds, in which the O(1) and O(2) atoms act as proton acceptors. It is noteworthy that the O(2) atom participates not only in the "intermolecular" hydrogen bonding, but also in the "intramolecular" N(1)–H···O(2) hydrogen bond as an acceptor.

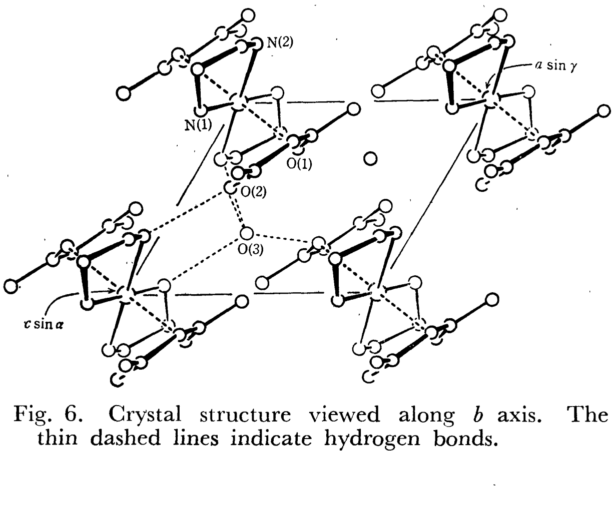

Fig. 6. Crystal structure viewed along *b* axis. The thin dashed lines indicate hydrogen bonds.

Table 6. Interatomic distances and angles related to the hydrogen bonds

A—H···B		A···B	H···B	A-H-B	Positions* of A	Positions* of B
N(1)	O(3)	2.97(1) Å	2.06 Å	153°	3	1
N(2)	O(2)	2.97(1)	2.12	142	4	1
N(2)	O(3)	3.04(1)	2.07	165	2	1
O(3)	O(1)	2.79(1)			1	5
O(3)	O(2)	2.83(1)			1	1
N(1)	O(2)	3.02(1)	2.02	175	1	1

Atoms A	Atoms B	Atoms C	A-B-C	Positions* of A	Positions* of B	Positions* of C
C(4)	O(1)	O(3)	109.3(7)°	5	5	1
C(6)	O(2)	O(3)	131.7(7)	1	1	1
C(6)	O(2)	N(2)	141.6(7)	1	1	4
N(2)	O(2)	O(3)	81.0(3)	4	1	1
N(1)	O(2)	N(2)	93.6(3)	1	1	4
N(1)	O(2)	O(3)	88.7(3)	1	1	1
N(1)	O(2)	C(6)	105.0(7)	1	1	1
O(1)	O(3)	O(2)	139.1(4)	5	1	1
O(1)	O(3)	N(2)	86.1(3)	5	1	2
O(1)	O(3)	N(1)	120.0(4)	5	1	3
O(2)	O(3)	N(1)	100.9(4)	1	1	3
O(2)	O(3)	N(2)	93.1(3)	1	1	2
N(1)	O(3)	N(2)	93.0(3)	3	1	2

* Numercials refer to the following equivalent positions:
1 *x*, *y*, *z* 2 –*x*, –*y*, –*z* 3 –*x*, –*y*, 1–*z*
4 *x*, *y*, 1+*z* 5 1–*x*, 1–*y*, 1–*z*

Experimental

Materials. The $Cu(acac)_2$[43] and $Cu(etac)_2$[44] were synthesized according to the literature and were recrystallized twice from benzene-chloroform and dichloromethane respectively. Commercial en and tn were distilled over metallic sodium just before use. Analytical-grade bipy and phen-monohydrate were used without further purification. The dichloromethane was purified by the usual methods described previously.[45] The diethyl ether was dried with calcium chloride and distilled over sodium. The mercury(II) tetraisothiocyanatocobaltate(II) was prepared according to Figgis and Nyholm[46] and used as a reference substance for the magnetic measurements (Found: C, 9.73; N, 11.39%).

Measurements. The IR spectra in the 4000—650 cm^{-1} region were measured with a Jasco IR-E Infrared Spectrophotometer, and those in the 700—250 cm^{-1} region, with a Hitachi grating infrared spectrophotometer EPI-L. The diffuse reflectance spectra were recorded with a Hitachi-Perkin Elmer 139 Spectrophotometer or a Hitachi EPU-2 Recording Spectrophotometer. The conductivity was measured by the use of a Yanagimoto Conductivity Outfit, NY-7. The magnetic susceptibilities were measured at room temperature by the Faraday method, with a Shimadzu Magnetic balance and employing mercury(II) tetraisothiocyanatocobaltate(II) as a reference substance. The diamagnetic corrections were calculated from Pascal's constants. The thermogravimetric analyses were performed using a thermo-spring-balance C-282 of Hamada Denki Seisakusho, Ltd., under reduced pressure. The rate of temperature elevation was fixed at 10 °C/hr.

Preparations of Complexes. *Bis(acetylacetonato)ethylenediaminecopper(II) Cu(acac)$_2$(en)*: To a solution of Cu(acac)$_2$ in dry dichloromethane, we added, drop by drop with magnetical stirring, a solution of equimolar en in dry dichloromethane. The pale-green precipitate thus produced was transferred from the reaction vessel *via* polyethylene tubing to a filtering apparatus set up in a desiccator containing phosphorus pentoxide. It was then recrystallized from dry benzene. Mp 112 °C (decomp.). The same compound was also prepared by the reaction of Cu(acac)$_2$ suspended in dry ether with equimolar en in dry dichloromethane.

The corresponding deuterated en complex was prepared by the following method: ethylenediamine-d_4 was prepared by repeated fractional distillation from heavy water solutions and characterized by means of its NMR spectra. Into a solution of 0.1 g of Cu(acac)$_2$ in 10 ml of dry dichloromethane, we stirred a few drops of en-d_4 until a small amount of pale green precipitate was formed. The precipitate thus produced was filtered rapidly and submitted to the measurement of its IR spectra.

Bis(ethyl acetoacetato)ethylenediaminecopper(II), Cu(etac)$_2$(en): This complex was prepared in a manner similar to that used for the corresponding acetylacetonate complex and was recrystallized from benzene. Mp 144 °C (decomp.).

Bis(ethyl acetoacetato)trimethylenediaminecopper(II), Cu(etac)$_2$(tn): To a solution of Cu(etac)$_2$ in dichloromethane, we added an equimolar amount of tn in dichloromethane. After a while a pale green precipitate was produced; this was filtered out and dried *in vacuo*. Mp 130 °C (decomp.).

Bis(ethyl acetoacetato) (2,2′-bipyridine)copper(II), Cu(etac)$_2$(bipy): About three times as many moles of bipy were added to a solution of Cu(etac)$_2$ in dichloromethane. After refluxing for 3 hr, the solvent was evaporated until a green powder was produced. The mixture was filtered, washed with acetone to exclude any unchanged materials, and dried *in vacuo*. Mp 124 °C (decomp.).

Bis(ethyl acetoacetato) (1,10-phenanthroline)copper(II), Cu(etac)$_2$(phen): A small excess of phen-monohydrate was added to a solution of Cu(etac)$_2$ in dichloromethane. After heating for about ten minutes, the solution was concentrated by evaporation under reduced pressure; then petroleum ether was added to the concentrate to produce a green precipitate. It was filtered and recrystallized from dichloromethane-petroleum ether. Mp 115 °C (decomp.).

Bis(ethylenediamine)copper(II) acetylacetonate dihydrate, [Cu(en)$_2$](acac)$_2$·2H$_2$O: Into a solution of Cu(acac)$_2$ in wet dichloromethane, we added, drop by drop with vigorous stirring, a solution containing two times as many moles of en in dichloromethane. A violet precipitate thus formed was filtered out and recrystallized from warm (below 50 °C) benzene containing a small amount of en. Mp 62 °C (decomp.).

X-ray-data Measurement. Parallelepiped crystals of [Cu(en)$_2$](acac)$_2$·2H$_2$O were obtained by recrystallization from a 1 : 1 mixture of benzene and dichloromethane containing a small amount of en. Because of the remarkable air- and moisture-sensitivity, crystals used for the X-ray work were sealed into thin-walled glass capillaries.

Crystal Data: $\mathrm{Cu(C_2H_8N_2)_2(C_5H_7O_2)_2 \cdot 2H_2O}$, $M=418$, triclinic, $a=7.730(7)$, $b=11.53(1)$, $c=7.007(7)$ Å, $\alpha=72.7(1)^\circ$, $\beta=121.8(1)^\circ$, $\gamma=100.2(1)^\circ$, $V=506.7$ Å^3, $Z=1$, $D_c=1.73$ g·cm^{-3} (D_m not measured, because of the instability of the crystal in air), $\lambda(\mathrm{Cu}K\alpha)=1.5418$ Å, $\mu(\mathrm{Cu}K\alpha)=19.6$ cm^{-1}; space group $P\bar{1}$ or $P1$, shown to be the former from the subsequent satisfactory solution and refinement of the structure.

The unit-cell dimensions were determined by a least-squares analysis of the $\sin^2\theta$ values from high-angle reflections on zero-level Weissenberg photographs calibrated with aluminum powder.

The intensity data were measured visually from equi-inclination Weissenberg photographs (layers $hk0$—5) by the multiple-film technique with Cu$K\alpha$ radiation. The crystal used for the collection of intensity data had dimensions of $0.7\times0.4\times0.2$ mm. Although preliminary data were recorded about the other axes, photographs suitable for intensity measurements could be obtained only about the c axis. Corrections were applied for the Lorentz and polarization factors and for the absorption. A total of 1550 independent reflections were obtained, of which 115 were too weak to be measured.

Determination and Refinement of the Crystal Structure. The positions of all the non-hydrogen atoms were found from a three-dimensional Patterson synthesis on the assumption that the space group was $P\bar{1}$. The atomic coordinates and thermal parameters were refined by the block-diagonal-matrix least-squares method, the function minimized being $\sum w(|F_0|-|F_c|)^2$. At every termination of several cycles of the least-squares calculation, the layer scales were calculated so that relative $\sum|F_0|=\sum|F_c|$ for each of the layers; the new scales thus obtained were then used in the following calculation.

TABLE 7. THE FINAL ATOMIC COORDINATES, TEMPERATURE FACTORS AND THEIR e.s.d.s.

Atom	x	y	z	B
Cu	0	0	0	*
N (1)	−0.135(1)	0.112(1)	0.045(1)	3.3(1)
N (2)	−0.059(1)	0.124(1)	−0.298(1)	3.2(1)
C (1)	−0.242(2)	0.209(1)	−0.175(2)	4.0(2)
C (2)	−0.115(2)	0.240(1)	−0.292(1)	3.5(2)
C (3)	0.482(2)	0.282(1)	0.050(2)	5.3(2)
C (4)	0.377(2)	0.246(1)	0.188(1)	3.6(2)
C (5)	0.318(2)	0.337(1)	0.233(2)	3.7(2)
C (6)	0.219(1)	0.322(1)	0.355(1)	3.3(1)
C (7)	0.161(2)	0.439(1)	0.375(2)	5.2(2)
O (1)	0.345(1)	0.133(1)	0.251(1)	4.1(1)
O (2)	0.162(1)	0.224(1)	0.444(1)	4.1(1)
O (3)	0.351(1)	−0.004(1)	0.692(1)	4.4(1)

* B_{11}	B_{22}	B_{33}	B_{12}
0.0263(6)	0.0076(1)	0.0286(5)	0.0073(4)

B_{13}	B_{23}
0.0349(8)	−0.0014(4)

The anisotropic thermal parameters for Cu atom is of the form

$$\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)].$$

Continued refinements ($w=1.0$ for all reflections) with isotropic temperature factors reduced R to 0.16. In the subsequent refinements, the following weighting scheme was employed:

$$w = 0.5 \text{ for } |F_0| < |F_{\min}|$$
$$w = 1.0 \text{ for } |F_{\min}| \leq |F_0| \leq |F_{\max}|$$
$$w = |F_{\max}|/|F_0| \text{ for } |F_{\max}| < |F_0|$$

$|F_{\max}|$ and $|F_{\min}|$ were varied as is indicated by the $|F_0|$ and $(\sin\theta/\lambda)$ analyses of $\sum w(|F_0|-|F_c|)^2$. Four further cycles of the calculation were made using anisotropic thermal parameters for the copper atom, and R was improved to 0.13. All the layer scales were almost invariant as compared with the preceding ones, the maximum change being within the range of one per cent. Four reflections, thought to be suffering from extinction errors (010, 111, 121, $\bar{1}$11), were omitted in the final refinement, which led to a convergence at R 0.12 ($|F_{\max}|=7.9$ and $|F_{\min}|=2.6$). In the final cycle of refinement, all the shifts were $<0.3\ \sigma$. The atomic scattering factors for neutral copper, oxygen, nitrogen, and carbon atoms, as well as the correction for the real part of the anomalous dispersion for the copper atom, were taken from Ref. 47. The final list of coordinates and thermal parameters is given in Table 7. A complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 7425). All the computations were carried out by means of the FACOM 270—30 computer at Osaka City University.[48]

The authors are indebted to Dr. H. Kobayashi of Kyoto University for her help in the magnetic measurements and also to Mr. J. Gohda for the elemental analyses. Financial aid by the Ministry of Education is also acknowledged.

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