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Mixed Copper Complexes of Some β-Diketones with α,α'-Dipyridyl[1]

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Cu-α,α'-dipyridyl(Cu-Dip) has two unoccupied coordination sites, and when acetylacetone, benzoylacetone, dibenzoylmethane, *p*-carboxydibenzoylmethane, trifluoroacetylacetone, benzoyltrifluoroacetone and salicylaldehyde were reacted on Cu-Dip respectively, the presence of two different equilibria in Chart 1 was suggested spectrophotometrically according to the ratio of Cu-Dip and β-diketone. These equilibria are: Cu-Dip+β-diketone⇄β-diketone-Cu-Dip, β-diketone-Cu-Dip+β-diketone⇄Cu(β-diketone)$_2$+Dip.

The isosbestic points which indicate the presence of the above equilibria respectively, were observed in the spectra of the mixed complexes. Furthermore, the study of the relation between the isosbestic points and β-diketone concentration to Cu-Dip revealed the relative reactivity for the formation of Cu(β-diketone)$_2$ which was shown in the order: dibenzoylmethane>benzoylacetone>acetylacetone>salicylaldehyde>*p*-carboxydibenzoylmethane≫trifluoroacetylacetone, benzoyltrifluoroacetone.

Mixed complexes of Cu(II) with α,α'-dipyridyl and β-diketone (1:1:1) were synthesized by reacting β-diketone to Cu-Dip in 50% dioxane solution containing 0.1M $NaHCO_3$.

It is well known that Cu(II) formes complexes with α, α'-dipyridyl (Dip) in the ratio of 1:1, 1:2 and 1:3, among which 1:1 complex is most stable.[3]

Cu-Dip (1:1) complex has been reported to have a catalytic ability on the hydrolysis of diisopropyl fluorophosphate (DFP)[4] and salicyl phosphate homologues (SP).[5] In these cases, the formation of mixed complexes among Cu, Dip and DFP or SP might be taken into consideration as the transition states during the hydrolysis, although they have not been isolated yet. As the coordination number of Cu(II) is ordinally four, Cu(II) ion of Cu–Dip(I) has still two unoccupied coordination sites. Therefore, it is probable that, if a certain complexing agent is added, I could form a mixed complex with the second ligand by utilizing the unoccupied sites of Cu(II) in the complex.

Acetylacetone was shown to form the mixed complex with Cu(II)-ethylenediamine by spectrophotometric investigation.[6] However, the mixed complex formation between β-diketone and I has not been reported.

In the present paper, the authors described the spectrophotometric studies on the interaction of β-diketones to I and on the syntheses of some mixed complexes. β-Diketones used here were as follows: acetylacetone (AA), benzoylacetone (BA), dibenzoylmethane (DBM), *p*-carboxydibenzoylmethane (CDM), trifluoroacetylacetone (TFA), benzoyltrifluoroacetone (BFA) and a phenolic aldehyde, salicylaldehyde (SA).

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[1] A part of this work was presented before in the 21st Annual Meeting of Pharmaceutical Society of Japan, Tokushima, October 1965.

[2] Location: *Yayoi-cho, Chiba-shi.*

[3] The Chemical Society of Japan (ed.), "Jikken Kagaku Koza," Coll. Vol. 11, Maruzen Co., Tokyo, 1959, p. 81.

[4] T. Wagner-Jauregg, *J. Am. Chem. Soc.*, 77, 922 (1955).

[5] A.E. Martell, *J. Phys. Chem.*, 67, 584 (1963).

[6] S. Kida, *Bull. Chem. Soc. Japan*, 29, 805 (1956).

Result and Discussion

Absorption Spectra

I shows a maximum of the absorption spectrum at 620 mμ. When β-diketone was added to I solution, the maximum absorption was lowered. This fact may be considered to be due to the mixed complex formation of the ketone with I or the substitution reaction of the ketone to I. Therefore, the molar ratio method was applied to clarify the stoichiometric relation of the reaction mentioned above.

In the case of I and AA, which is shown in Table I and Fig. 1 and 2, it was found that the intersecting point determined interpolately appeared in the region between 1 and 2 of the molar ratio of AA to I, and two isosbestic points A and B were present in the absorption spectra.

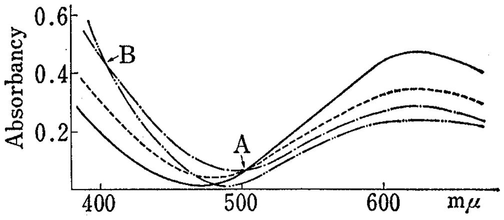

Fig. 1. Effect of Molar Ratio of Cu-Dip and AA to Absorption Spectra

spectrum	Cu-Dip : AA
———	1 : 0
-----------	1 : 0.5
—·—·—	1 : 1
—··—··	1 : 2

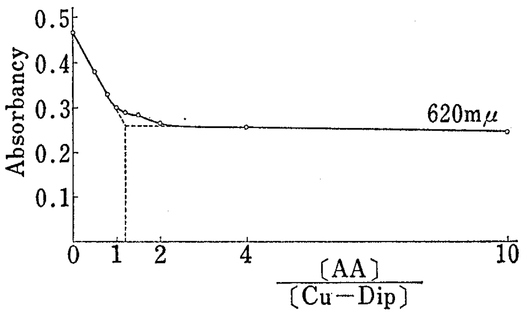

Fig. 2. Effect of Varying Concentration Ratio of AA to Cu-Dip

Table I. Molar Ratio Method for I and AA

I:AA	I c_1 (ml)	AA c_2 or c_3 (ml)	Solvent (ml)	Isosbestic point
1:0	5	0	5	A
1:0.5	5	c_2 2.5	2.5	A
1:0.8	5	c_2 4.0	1.0	A
1:1.0	5	c_2 5.0	0	A, B
1:1.2	5	c_3 0.6	4.4	B
1:1.5	5	c_3 0.75	4.25	B
1:2	5	c_3 1.0	4.0	B
1:4	5	c_3 2.0	3.0	B
1:10	5	c_3 5.0	0	B

concentration : c_1, c_2 10^{-2}M; c_3 10^{-1}M

Isosbestic point A was observed in the spectra of the ratio of AA to I 0—1, while isosbestic point B was in the ratio of AA to I 1—10. At AA to I 1:1, both of the isosbestic points were clearly observed. The presence of the two isosbestic points strongly suggests that two different equilibria may be involved in the complex formation of I and AA, and this assumption was supported partly by the experimental fact that the isolation of AA–Cu–Dip was achieved from the solution of AA to I 1:1, and $Cu(AA)_2$ was obtained from the solution of AA to I 10:1. Therefore, it may be reasonable to consider the isosbestic point A suggests the equilibrium (1), while the point B corresponds to the equilibrium (2) as is seen in Chart 1.

The molar ratio studies of the other mixed complexes were carried in the similar manner as described at I and AA, and Fig. 3 and 4 show the spectra for I and DBM, and I and TFA, respectively. Their spectral behaviors were found similar to those of I and AA, however,

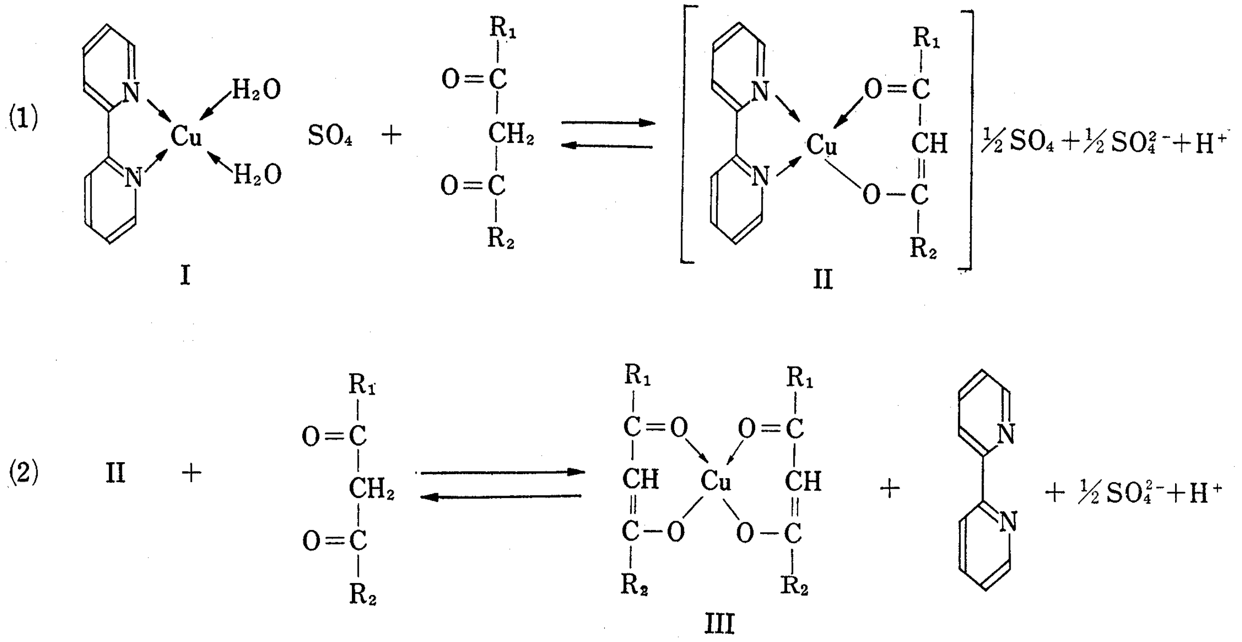

Chart 1

in any case of DBM, TFA, and BFA, isosbestic point B was not observed since $Cu(DBM)_2$ precipitated and $Cu(TFA)_2$ and $Cu(BFA)_2$ were not obtained in the experimental conditions. Isosbestic points A and B of the mixed complexes studied here are summarized in Table II.

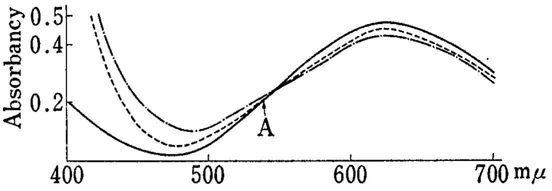

Fig. 3. Effect of Molar Ratio of CuDip and DBM to Absorption Spectra

spectrum	Cu-Dip : DBM
———	1 : 0
-----------	1 : 0.3
—·—·—	1 : 0.4

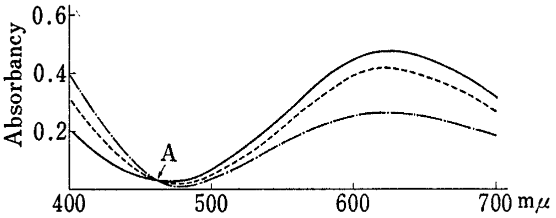

Fig. 4. Effect of Molar Ratio of Cu-Dip and TFA to Absorption Spectra

spectrum	Cu-Dip : TFA
———	1 : 0
-----------	1 : 1
—·—·—	1 : 10

Table II. Wavelength of Isosbestic Points A and B of the Mixed Complex of β-Diketone with I

β-Diketone	Isosbestic point A(mμ)	Isosbestic point B (mμ)
AA	500	410
BA	508	499
DBM[a)]	538	—
CDM	528	514
SA	668, 570	532
TFA[b)]	460	—
BFA[c)]	486	—

a), b), c) Isosbestic point B was not observed.

Syntheses of Mixed Complexes

Seven mixed complexes were synthesized by the reaction of β-diketones and salicyl aldehyde with I. The information obtained from the spectral studies described above were found quite useful to establish the experimental conditions which were given in the experimental part of this paper.

Infrared Spectra

Infrared spectrum (IR) of the synthesized AA-Cu-Dip was compared with those of AA, Dip, I and $Cu(AA)_2$ in order to investigate whether AA-Cu-Dip has chelation bonding in its structure. As is seen in Fig. 5, an absorption band at 1580 cm^{-1} of Dip moves to 1600 cm^{-1} in I, and at the same position the product has also a strong absorption. This relationship indicates that the chelation bonding exists between Cu and Dip in the mixed complex. In addition, AA has a strong absorption at 1620 cm^{-1} where the product has no absorption, however the product has strong absorption at 1540 cm^{-1} and 1580 cm^{-1}, where $Cu(AA)_2$ has its absorption. From this result, the chelation bonding may be possible between Cu and AA in the mixed complex. Furthermore, the product has also a strong and broad absorptnio assignable to SO_4^{2-} at 1100 cm^{-1}, and this band indicates that the mixed complex holds SO_4^{2-} in its structure.

The structural formula (II) in Chart 1 is then proposed to be the most reasonable one for β-diketone-Cu-Dip complex from these data.

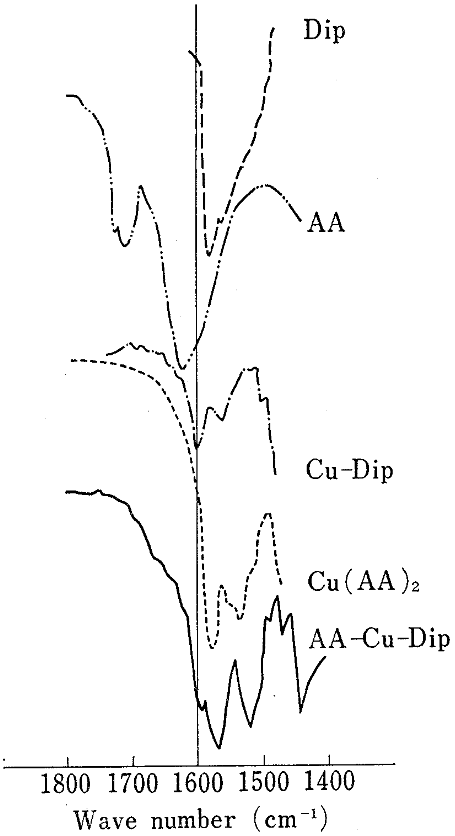

Fig. 5. IR Spectra

Ultraviolet Absorption

Ultraviolet absorption (UV) spectra were measured for the methanolic solutions of I, the synthesized mixed complexes and copper chelates of β-diketones. All copper β-diketonates were synthesized under the condition of the ratio of copper to β-diketone 1:2 preceding to the spectral measurement. As is seen in Table III, the characteristic λ_{max} of I are observed at 301 mμ and 311 mμ, which are not found in the copper chelates of BA, BFA, and DBM. Copper chelates of AA and TFA have λ_{max} at 295 mμ and 297 mμ, respectively, and both mixed complexes of these β-diketones with I have new λ_{max} at 298 mμ and 310 mμ (shoulder). The mixed complexes of BA, BFA, and DBM with I have four λ_{max} at 250—260 mμ, near 300 mμ, 310 mμ and around 330—350 mμ. Since the copper chelates of BA, BFA and DBM show λ_{max} in the range of 255—270 mμ and 324—356 mμ, it is clearly seen that both of the characteristic ultraviolet absorption feature found in I and the copper chelates of the diketones mentioned above are completely retained in the spectra of the mixed complexes. Therefore, the investigation of the λ_{max} in the ultraviolet absorption spectra of these mixed complexes may be useful to consider the structures of the mixed complexes of these types.

Relative Reactivity of the Mixed Complexes for Substitution

From the spectral study of the mixed complexes mentioned above, it may be deduced that the mixed complex reaction would have at least two steps; (1) mixed complex formation and (2) substitution reaction according to the molar ratios of β-diketones to I. And isosbestic

Table III. Ultraviolet Absorption

Material	$\lambda_{\max}^{\text{methanol}}$ (mμ)			
I	245	301	311	
AA-Cu-Dip		298	310sh	
Cu(AA)$_2$	244	295		
TFA-Cu-Dip		298	310sh	
Cu(TFA)$_2$	236	297		
BA-Cu-Dip	250	300	310	332
Cu(BA)$_2$	255			324
BFA-Cu-Dip	250	300	310	335
Cu(BFA)$_2$	270			330
DBM-Cu-Dip	260	299	310	350
Cu(DBM)$_2$	266			356
SA-Cu-Dip	260	298	310	
Cu(SA)$_2$	242 255 279sh			324

sh, shoulder

points A and B can be considered as the criterions of both (1) and (2), respectively. The molar ratio of β-diketone to I at which the isosbestic points A and B appear is not the same for all mixed complex reactions, and depends on the reactivity of β-diketones to I. In the case of I and DBM, isosbestic point A was observed until the ratio of DBM to I 0.3:1, while I and TFA or BFA did not show the point B even in high ratio of the diketone to I 10:1, and hence the reaction (2) could not be observed at the experimental conditions. The molar ratios related to the isosbestic points A and B of the other β-diketones to I were found to fall between the ratio of DBM and TFA, and BFA. Therefore, if it is assumed that molar ratio defined above indicates the relative reactivity of the β-diketone to I, then the following order will be obtained for the β-diketones studied here in the mixed complex reaction; DBM(0.3)$>$BA(0.8)$>$AA(1.0)$>$SA(1.3)$>$CDM(1.7)$\gg$ TFA, BFA. The value in parenthesis means the molar ratio at which the substitution reaction (2) begins. As is seen in Table IV, this order of reactivity agrees well with the order of pK_a of the β-diketones, and resembles to the tendency of stability constants of copper complexes of the diketones measured in 75% dioxane at 30°.

Table IV. pK_a fo Some β-Diketones and Stability Constants of Their Copper Complexes

β-Diketone	pK_a	log K	Temperature(°C)	Solvent
AA[a]	12.75	23.66(k_1k_2)	30	75% dioxane
TFA[b]	8.70	17.2 (k_1k_2)	30	75% dioxane
BA[b]	12.85	23.01(k_1k_2)	30	75% dioxane
BFA[b]	6.00	18.8 (k_1k_2)	30	75% dioxane
DBM[c]	13.75	24.98(k_1k_2)	30	75% dioxane

a) R.M. Izatt, W.C. Fernelius, B.P. Block, *J. Phys. Chem.*, **59**, 80 (1955)
b) L.G. Van Uitert, W.C. Fernelius, B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953)
c) *Idem., ibid.*, **75**, 2736 (1953)

Experimental

Apparatus——Spectra were taken by Hitachi EPS-3T autorecording spectrophotometer. IR spectra were measured by Nippon Bunko IRS autorecording spectrophotometer with KBr. Toa Dempa HM-5A pH meter was used for the measurement of pH of sample solutions.

Materials and Reagents——$CuSO_4 \cdot 5H_2O$, α,α'-dipyridyl(Dip) and $NaHCO_3$ were of analytical grade. Acetylacetone (AA) was purchased from Dojindo Co., Ltd., Research Laboratories and was shaken with a tenth part of diluted NH_4OH (1:10), washed with water, dried, and distilled at 140—142°. Benzoylacetone (BA), dibenzoylmethane (DBM), salicylaldehyde (SA), trifluoroacetylacetone (TFA), and benzoyltrifluoroacetone (BFA) were also obtained from the same laboratories. *p*-Carboxydibenzoylmethane (CDM) was synthesized by the method of Smedley.7) Dioxane of extra pure grade was purified by the ordinary method. Solvent for the spectral measurements and the syntheses of the mixed complexes except the case of SA-Cu-Dip was prepared by dissolving $NaHCO_3$ in 50% aqueous dioxane to 0.1M solution and adjusted to pH 9.6.

I was synthesized by reacting $CuSO_4 \cdot 5H_2O$ with Dip, and recrystallization from boiling water gave needles charred between 168—175°. *Anal.* Calcd for $C_{10}H_{12}O_6N_2SCu$: C, 34.14; H, 3.44; N, 7.96. Found: C, 33.73; H, 3.30; N, 7.70.

Molar Ratio Method——I and β-diketones were dissolved in the solvents respectively, and were mixed together to make solutions having various ratios of β-diketones to I. Spectral measurements were performed on the solutions after being equilibrated for 30 min at room temperature. Details of the experiment for I and AA are presented in Table I.

Syntheses of Mixed Complexes——AA-Cu-Dip (1:1:1): 700 mg of I (2×10^{-3} mole) was dissolved in 200 ml of solvent, to which 0.2 ml of AA (2×10^{-3} mole) was added with stirring at room temperature. The reaction mixture was shaken with *n*-butanol after addition of NaCl. After removing the aqueous phase, ether was added to the butanol phase to get the precipitates. The precipitates obtained were dried over $CaCl_2$ *in vacuo*, washed with ether and dried again. The product was dissolved in anhydrous MeOH to remove inorganic impurities by filtration. A greenish blue crystal, mp 191° was obtained on concentration of the methanol solution. *Anal.* Calcd. for $C_5H_7O_2$–Cu–$C_{10}H_8N_2 \frac{1}{2} SO_4$: C, 49.10; H, 4.12; N, 7.64; Cu, 17.32. Found: C, 49.06; H, 4.15; N, 7.96; Cu, 17.18.

BA-Cu-Dip (1:1:1): 176 mg of I (5×10^{-4} mole) was reacted with 65 mg of BA (4×10^{-4} mole) in almost the same procedure as described in AA-Cu-Dip. A dark green crystal, mp 142° was obtained on recrystallization from *n*-propanol. *Anal.* Calcd. for $C_{10}H_9O_2$–Cu–$C_{10}H_8N_2 \frac{1}{2} SO_4$: C, 53.74; H, 4.29; N, 6.27; Cu, 14.22. Found: C, 54.02; H, 4.34; N, 6.79; Cu, 14.25.

DBM-Cu-Dip (1:1:1): To a solution of 281.5 mg of I (8×10^{-4} mole) in 80 ml of the solvent, 44.9 mg of DBM (2×10^{-4} mole) in 10 ml of the solvent was added with vigorous stirring for 30 min at room temperature. The reaction mixture was washed with ether to remove unreacted DBM, and the product was extracted with *n*-butanol and washed with water. After removing water with anhydrous Na_2SO_4, the butanol phase was evaporated to dryness. A green crystal, mp 234° was obtained by recrystallization from MeOH and ether. *Anal.* Calcd. for $C_{15}H_{11}O_2$–Cu–$C_{10}H_8N_2 \frac{1}{2} SO_4$: C, 61.95; H, 3.94; N, 5.71; Cu, 12.94. Found: C, 62.37; H, 4.91; N, 5.16; Cu, 12.82.

CDM-Cu-Dip (1:1:1): To a solution of 176 mg of I (5×10^{-4} mole) in 50 ml of the solvent, 134 mg of CDM (5×10^{-4} mole) in 30 ml of the solvent was added at room temperature with constant stirring. The solution was concentrated under reduced pressure at 40° until a precipitate formed. Then the solution was kept in a refrigerator over night, and the precipitate was filtered, washed with water, dried *in vacuo*, and finally washed with ether and dried over $CaCl_2$. A dark yellowish green crystal, mp 220° was obtained. *Anal.* Calcd. for $C_{16}H_{12}O_4$–Cu–$C_{10}H_8N_2 \frac{1}{2} SO_4$: C, 61.84; H, 4.19; N, 5.55; Cu, 12.88. Found: C, 61.57; H, 3.86; N, 5.84; Cu, 11.55.

TFA-Cu-Dip (1:1:1): 105.6 mg of I (3×10^{-4} mole) in 30 ml of the solvent was mixed with 462.2 mg of TFA (3×10^{-3} mole) in 30 ml of the solvent and the mixture was stirred for 30 min at room temperature. The product was then extracted with benzene, and benzene phase was washed with water. The benzene solution was dried and evaporated to dryness, and the residue was dissolved in absolute MeOH to remove undissolved inorganic impurities. Recrystallization from MeOH gave a yellowish green crystal, mp 160°. *Anal.* Calcd. for $C_5H_4O_2F_3$–Cu–$C_{10}H_8N_2 \frac{1}{2} SO_4$: Cu, 15.32. Found: Cu, 15.30.

BFA-Cu-Dip (1:1:1): 176 mg of I (5×10^{-4} mole) in 50 ml solvent was mixed with 1082 mg of BFA (5×10^{-3} mole) in 10 ml of the solvent and treated in the same manner as described in TFA-Cu-Dip. A yellowish green crystal, mp 195—197° was obtained on recrystallization from aqueous MeOH. *Anal.* Calcd. for $C_{10}H_6O_2F_3$–Cu–$C_{10}H_8N_2 \frac{1}{2} SO_4$: Cu, 13.16. Found: Cu, 12.75.

SA-Cu-Dip (1:1:1): To a solution of 509 mg of I (1.4×10^{-3} mole) in 50 ml of 0.1M $NaHCO_3$ aqueous solution, 0.15 ml of SA (1.4×10^{-3} mole) was added at room temperature under stirring. Until a deep green crystal began to appear, NaCl was added and then the solution was kept in a refrigerator for a night. A dark green crystal, mp 200—201° was obtained. *Anal.* Calcd. for $C_7H_5O_2$–Cu–$C_{10}H_8N_2 \frac{1}{2} SO_4$: C, 52.37; H, 3.62; N, 7.18; Cu, 16.30. Found: C, 51.81; H, 3.66; N, 7.28; Cu, 16.40.

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