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Synthesis, Characterization, and Crystal Structure of Substituted Derivatives of (Tetraazacyclotetradecatetraenato)copper(II) Complexes

Naohide MATSUMOTO,* Masahiko IMAIZUMI, and Akira OHYOSHI

Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860

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(Tetraazacyclotetradecatetraenato)copper(II) complexes with the general formula [Cu(Me$_2$E$_2$[14]tetraenatoN$_4$)], where E denotes the substituent group of acetyl, propionyl, isobutyryl, benzoyl, *p*-methylbenzoyl, or *p*-nitrobenzoyl, have been prepared *via* electrophilic substitution of the parent complex [Cu(Me$_2$[14]tetraenatoN$_4$)] with acid chlorides, and characterized by elemental analyses and infrared spectra. For the *p*-substituted benzoyl derivatives, both the position of d-d electronic band maxima and reduction potential assignable to $Cu^{2+}+e \rightarrow Cu^+$ vary linearly with the Hammett substituent constants. The crystal structure of one of the complexes [Cu(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)]·H$_2$O has been determined by the single-crystal X-ray diffraction method. The copper atom assumes a square planar coordination geometry and the overall conformation of the complex assumes a chair-like shape, where the seat and the rests are formed by the coordination plane (CuN$_4$) and the two conjugated six-membered chelate rings respectively.

Kadish and Morrison[1–3] examined substituent effects in porphyrin complexes by substituting various groups at the para position of the phenyl rings of tetraphenylporphyrin. Busch and co-workers[4,5] reported syntheses of a broad range of substituted derivatives [Ni(Me$_2$E$_2$[Z]tetraenatoN$_4$)] (Z=14, 15, 16) by electrophilic substitution at the γ-carbon of the conjugated chelate rings (Fig. 1), and examined substituent effects on electronic spectral and electrochemical properties of the complexes. These studies elucidated that the use of substituents affords a powerful technique for controlling the electronic character of the metal ion without altering the stereochemistry of the coordination sphere.

In this study, we have prepared the substituted derivatives [Cu(Me$_2$E$_2$[14]tetraenatoN$_4$)] by electrophilic substitution of the parent complex [Cu(Me$_2$[14]tetraenatoN$_4$)] with acid chlorides such as propionyl chloride, isobutyryl chloride, benzoyl chloride, *p*-methylbenzoyl chloride, and *p*-nitrobenzoyl chloride. These complexes were characterized by elemental analyses and infrared spectra. Substituent effects on the properties of the copper ion were examined by electronic spectra and cyclic voltamogram. In addition, the crystal structure of [Cu(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)]·H$_2$O has been determined by the single-crystal X-ray diffraction method in order to confirm the basic structure for the series of complexes.

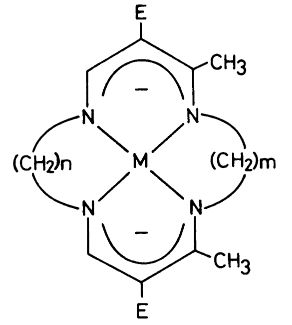

Fig. 1. Structure of [M^{2+}(Me$_2$E$_2$[Z]tetraenatoN$_4$)], where E and Z denote the substituted group and the macrocyclic ring size, respectively. (Z=14(n=m=2), Z=15(n=2, m=3), Z=16(n=m=3)) The abbreviations used in this report are based on Busch's modified scheme.[6,7]

Experimental

Physical Measurements. Visible and ultraviolet spectra were recorded with a Hitachi recording spectrophotometer 323, while infrared spectra were recorded as KBr disk or nujol mull with a Shimadzu recording spectrophotometer IR-410. Elemental analyses were performed by Mr. Miyazaki at the Technical Service Center of Kumamoto University. Electrochemical measurements were performed with a Hokuto Denko Potentiostat/Galvanostat HA 101, a Hokuto Denko Function Generator HA 1074A, and a Rikadenki X-Y recorder BW-133. All measurements were made on acetonitrile solution containing 50 mM (1 M=1 mol dm^{-3}) tetrabutylammonium perchlorate as the supporting electrode. The working electrode was platinum disk electrode formed by sealing an 18—20 gauge platinum wire into soft glass. The reference electrode was a silver wire immersed in a 10 mM acetonitrile solution of silver perchlorate. Argon gas was bubbled into the solution for 30 min before measurement.

Syntheses. The acylated complex [Cu(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)]·H$_2$O was synthesized by the method of Jäger[8] or Riley and Busch.[9] Found: C, 50.09; H, 6.37; N, 14.59%. Calcd for C$_{16}$H$_{24}$N$_4$O$_3$Cu: C, 50.06, H, 6.30; N, 14.59%. IR (KBr): 1620 (C=O) and 1565 cm^{-1} (iminate ring).

(7,12-Dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)copper(II), [Cu(Me$_2$[14]tetraenatoN$_4$)]: This complex was first synthesized by Okawa and Busch[10] through a two-step procedure, in which the first step is removal of the acetyl groups along with the central nickel(II) ion and the second is reintroduction of the metal ion. In this work, this compound was synthesized through a one-step procedure by a similar method for the preparation of the corresponding nickel(II) complex.[5] In a 500 ml single-necked flask are combined 19.2 g (0.5 mol) of the complex [Cu(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)]·H$_2$O, 9.5 g (0.5 mol) of *p*-toluenesulfonic acid monohydrate, and 150 ml of methanol. The mixture is refluxed under nitrogen for 30 min, during which time the solution becomes dark red. The solution is then cooled in a Dry Ice/acetone bath and a solution of 4 g (0.1 mol) of sodium hydroxide in 50 ml of methanol is added under nitrogen, during which time the solution becomes green. The solution is removed from the cold bath and maintained for 30 min at room temperature. The methanol is removed dy evaporation to dryness, and 50 ml of dry benzene is added. The resulting slurry is filtered quickly by a glass filter. The solution is

evaporated to dryness to give a greenish material. Found: C, 50.81; H, 6.50; N, 19.53%. Calcd for $C_{12}H_{18}N_4Cu$: C, 51.14; H, 6.44; N, 19.88%. The complex decomposes gradually even in the solid state under atmosphere, in which the color changes from green to black.

The synthesis of the substituted complexes is exemplified in detail by that of [Cu(Me$_2$Bzyl$_2$[14]tetraenatoN$_4$)], because the synthetic procedure is similar to one another.

(6,13-Dibenzoyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)copper(II), [Cu(Me$_2$Bzyl$_2$[14]tetraenatoN$_4$)]: Benzoyl chloride of 0.15 g (10.6 mmol) is added to a solution of 1 g (3.5 mmol) of the deacetylated complex and 1.45 g (14.4 mmol) of triethylamine in 40 ml of dichloromethane and 40 ml of benzene. The mixture is stirred and refluxed under nitrogen for 4 h. The solvent is removed by evaporation and the residue is dissolved in 50 ml of chloroform, and filtered. The volume of the solution is reduced and the solution is chromatographed on a column of Merck 60G (ϕ2.0×20 cm^2) with chloroform as the eluent. The eluent of the first band is collected and the solvent is evaporated. Recrystallization is carried out in methanol to give red crystals. Found: C, 63.45; H, 5.27; N, 11.23%. Calcd for $C_{26}H_{26}N_4O_2Cu$: C, 63.72; H, 5.35; N, 11.43%. IR(KBr): 1618 (C=O), 1560 (iminate ring), and 1596 cm^{-1} (benzoyl group).

(6,13-Dipropionyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)copper(II), [Cu(Me$_2$Propi$_2$[14]tetraenatoN$_4$)]: Propionyl chloride of 0.99 g (10.67 mmol) was used instead of benzoyl chloride. Found: C, 54.70; H, 6.37; N, 13.87%, Calcd for $C_{18}H_{26}N_4O_2Cu$: C, 54.87; H, 6.65; N, 14.22%. IR(KBr): 1618 (C=O) and 1560 cm^{-1} (iminate ring).

(6,13-Diisobutyryl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)copper(II), [Cu(Me$_2$iso-Butryl$_2$[14]tetraenato-N$_4$)]: Isobutyryl chloride of 1.14 g (10.67 mmol) was used instead of benzoyl chloride. Found: C, 56.80; H, 7.26; N, 13.19%. Calcd for $C_{20}H_{30}N_4O_2Cu$: C, 56.92; H, 7.16; N, 13.27%. IR(KBr): 1630 (C=O) and 1575 cm^{-1} (iminate ring).

*(6,13-Bis(*p*-methylbenzoyl)-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)copper(II), [Cu(Me$_2$p-MeBzyl$_2$-[14]tetraenatoN$_4$)]*: *p*-Methylbenzoyl chloride of 1.65 g (10.67 mmol) was used instead of benzoyl chloride. Found: C, 64.72; H, 5.46; N, 10.34%. Calcd for $C_{28}H_{30}N_4O_2Cu$: C, 64.91; H, 5.83; N, 10.81%. IR(KBr): 1618 (C=O), 1550 (iminate ring), and 1600 cm^{-1} (benzoyl group).

*(6,13-Bis(*p*-nitrobenzoyl)-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)copper(II) Methanol, [Cu(Me$_2$p-NitroBzyl$_2$[14]tetraenatoN$_4$)]·CH$_3$OH*: *p*-Nitrobenzoyl chloride of 1.98 g (10.67 mmol) was used instead of benzoyl chloride. Found: C, 52.76; H, 4.76; N, 14.04%. Calcd for $C_{26}H_{24}N_6O_6Cu\cdot(CH_3OH)$: C, 52.98; H, 4.61; N, 13.73%. IR(KBr): 1620 (C=O), 1560 (iminate ring), and 1595 cm^{-1} (benzoyl group).

X-Ray Diffraction. The crystals of [Cu(Me$_2$Acyl$_2$[14]-tetraenatoN$_4$)]·H$_2$O were grown from a 98% methanolic solution as red prismatic crystals. The cell dimensions were determined by a least-squares method based on the angular settings of 15 reflections measured on a Syntex P$\bar{1}$ automated four-circle diffractometer. Intensity data were also collected with the diffractometer by a θ-2θ scan technique with a variable scan rate from 4.0 to 24.0°min^{-1}. The crystal data obtained are as follows: $C_{16}H_{22}N_4O_2Cu\cdot H_2O$, F.W.=383.9, triclinic system, space group=P$\bar{1}$, a=10.641(5), b=10.649(4), c=7.548(3) Å, α=90.98(3), β=88.95(3), γ=87.59(3)°, V=854.3 Å^3, D_m=1.46 (in KI aqueous solution), D_x=1.48 g cm^{-3} for Z=2, and μ(Mo $K\alpha$)=13.0 cm^{-1}. A total of 1597 independent reflections with $2\theta \leqq 42°$ were collected and these data were corrected for Lorentz and polarization effects, but not for absorption.

Structure Determination. Structure was solved by the conventional heavy-atom method and refined by the block-diagonal least-squares method. The function minimized in the procedure of the least-squares method was $\sum w(|F_o|-k|F_c|)^2$, where $w=1$ was adopted. The atomic scattering factors for Cu, O, N, C$_{\mathrm{cov}}$, and H were taken from the International Tables for X-ray Crystallography.[11] The anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for Cu were also taken from the literature.[11] All the calculation was carried out on a FACOM M-190 computer at the Computer Center of Kyushu University by the use of UNICS II program system.[12–14]

The coordinates of the copper atom were determined from a three-dimensional Patterson synthesis. Successive Fourier and difference Fourier syntheses revealed all the nonhydrogen atoms. Refinement was carried out by introducing initially isotropic thermal parameters and then anisotropic ones. At this stage, a difference Fourier synthesis was calculated and revealed all the hydrogen atoms except for those of water molecule. These hydrogen atoms were included in the refinement and gave the final value of 6.45% for $R=\sum||F_o|-|F_c||/\sum|F_o|$. The final difference Fourier synthesis showed four diffuse peaks (0.6 eÅ^{-3}) around the copper atom, but the other peaks are in the range −0.2 to 0.2 eÅ^{-3}. Final positional parameters with their estimated standard deviations are given in Table 1. Lists of structure factors, anisotropic thermal parameters, atomic parameters of hydrogen atoms, and selected least-squares planes have been deposited at the Chemical Society of Japan as Document No. 8245.

Results and Discussion

Crystal Structure of [Cu(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)]·H$_2$O. Perspective drawings with the atom numbering scheme, bond distances, and angles are shown in Fig. 2. The

TABLE 1. FRACTIONAL ATOMIC COORDINATES
All values have been multiplied by 10^4.

Atom	x/a	y/b	z/c
Cu	4344(1)	4343(1)	2498(2)
O(1)	7343(7)	213(7)	526(11)
O(2)	220(7)	7350(7)	4478(11)
N(1)	4312(7)	2539(7)	2386(11)
N(2)	6094(7)	4372(7)	2361(11)
N(3)	4415(7)	6116(7)	2622(11)
N(4)	2558(7)	4359(7)	2626(11)
C(1)	5345(9)	1735(9)	2113(13)
C(2)	6544(9)	2149(9)	1787(13)
C(3)	6888(9)	3428(9)	1955(13)
C(4)	6622(10)	5627(10)	2651(16)
C(5)	5615(10)	6607(10)	2313(16)
C(6)	3396(9)	6871(9)	3076(13)
C(7)	2170(9)	6569(9)	3219(13)
C(8)	1728(9)	5313(10)	2857(13)
C(9)	2098(10)	3093(10)	2228(15)
C(10)	3110(10)	2118(9)	2771(15)
C(11)	8902(10)	1659(11)	1041(16)
C(12)	7569(10)	1284(9)	1078(14)
C(13)	5118(12)	355(10)	2526(16)
C(14)	1650(11)	8908(10)	3957(16)
C(15)	1280(9)	7547(10)	3919(13)
C(16)	366(10)	5114(10)	2487(15)
O(3)	8104(9)	8117(9)	2517(18)

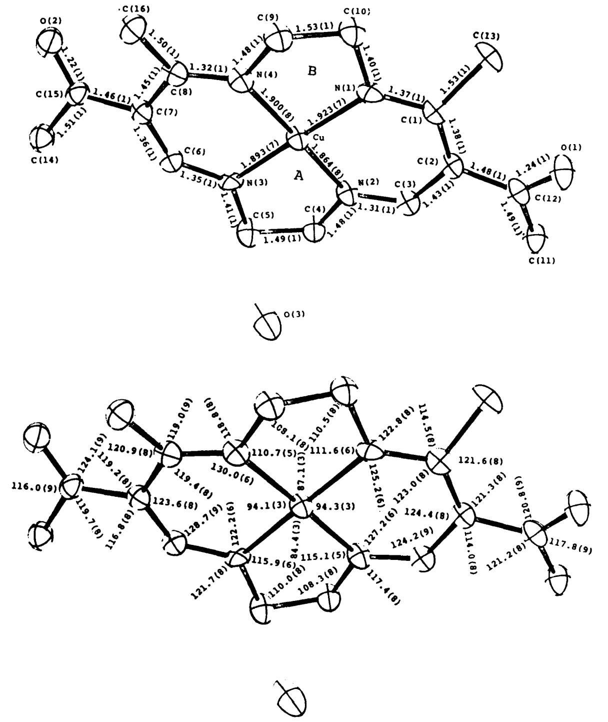

Fig. 2. ORTEP drawing of [Cu(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)]·H$_2$O with the atom numbering scheme, bond distances and angles. The thermal ellipsoids are drawn at 25% probability level. The hydrogen atoms are omitted for clarity.

crystal structure consists of a discrete neutral complex [Cu(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)] and a water molecule as crystal solvent. The copper atom is coordinated by four nitrogen atoms and the deviations of the component atoms from the coordination plane CuN$_4$ are in the range from −0.08 to +0.08 Å, showing a good planarity. The Cu–N bond distances are in the range expected for those of Cu–N(iminate)[15] and considerably shorter than those of the Cu–N (amine).[16]

For the two unsaturated six-membered chelate rings, the planarity for each chelate ring seems to be preserved, in which the deviations of the component atoms from the plane N$_2$C$_3$ are in the range from 0.05 to −0.03 Å. However, the C(13) of the methyl group bonded to C(1) deviates by 0.50 Å from the plane N$_2$C$_3$, due to the steric repulsion between the oxygen atom of the acyl group and itself. The C–C and C–N bond distances of the unsaturated chelate rings are intermediate between the corresponding single and double bond distances,[17] respectively, indicating that the chelate rings are π-electron conjugated systems. The saturated five-membered chelate rings (A and B) are all found to assume the gauche conformation with absolute configuration $\lambda\delta$ or $\delta\lambda$, where C(4) and C(5) deviate by 0.17 and −0.17 Å from the plane of CuN(2)N(3) and C(10) and C(9) deviate by 0.25 and −0.27 Å from the plane of CuN(1)N(4), respectively.

As a consequence of the planarities of the two conjugated chelate rings and the combination of the absolute configurations of the two saturated five-membered chelate rings, the overall conformation of the complex takes a chair-like shape, where the seat and the rests are formed by the coordination plane CuN$_4$ and the two unsaturated six-membered chelate rings, respectively. In other words, the two conjugated chelate rings are folded upward and downward on the CuN$_4$ plane with a gradient of 8°. This molecular conformation is apparently different from the so-called saddle shape conformation, which is observed in the analogous complexes with fifteen[18] and sixteen[19] membered ring sizes and in which the two unsaturated chelate rings are folded upward on the same side of the MN$_4$ plane.

Synthesis and Characterization. The complex [Cu(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)] can be converted into a powerful nucleophile by removal of the acetyl groups. The unsubstituted complex [Cu(Me$_2$[14]tetraenatoN$_4$)] reacts with a variety of electrophiles to produce derivatives that are substituted at the γ and γ' positions. The complexes with substituted groups at the γ and γ' positions were characterized by elemental analyses and infrared spectra. Infrared spectra showed the C=O stretching band in *ca.* 1620 cm^{-1} and the band of the iminate rings in *ca.* 1550—1580 cm^{-1}. Two vibrations (*ca.* 1770 and 1740 cm^{-1}) due to the C=O stretching of the starting material, *i.e.*, acid chlorides, are absent in products, supporting the introduction of the substituent.

Electronic Spectra. Visible and ultraviolet spectra of the complexes were obtained on 10^{-4}—10^{-5} mol dm^{-3} solutions in chloroform over the range (14—48)×10^3 cm^{-1}, and the band maxima are given in Table 2. The complexes show band maxima in the ultraviolet region with extinction coefficients in the range from 20000 to 48000 dm^3 mol^{-1} cm^{-1} which agree with the assignment of the band as representing a charge-transfer transition. The spectrum also exhibits a broad band in the visible region with an extinction coefficient in the range 400—750 dm^3 mol^{-1} cm^{-1} which is attributable to the d-d transition band.

Effect of electronic properties of the substituent groups was observed in the d-d transition band rather than in the charge-transfer band. The energy of the d-d transition increases with an increase in electron-withdrawing strength of the substituent groups, which is consistent with the result of Busch and co-workers[4,5] reported for nickel(II) complexes with a broad range of substituent groups in the same ligand system. For the complexes with *p*-substituted benzoyl groups, the observed d-d band maxima are linearly correlated to the Hammett substituent constants of the *p*-substituted groups, as shown in Fig. 3. This may be a result of the

TABLE 2. ELECTRONIC ABSORPTION BANDS FOR THE SUBSTITUTED DERIVATIVES [Cu(Me$_2$E$_2$[14]TETRAENATON$_4$)]

Substituent(E)	d-d Transition $\tilde{\nu}/10^3$ cm$^{-1}(\varepsilon)$	Other transition $\tilde{\nu}/10^3$ cm$^{-1}(\varepsilon)$
CH_3CO–	17.88(408)	31.87(47300)
C_2H_5CO–	17.79(395)	31.68(42600)
i-C_3H_7CO–	17.73(462)	31.74(39300)
p-$NO_2C_6H_4CO$–	18.52(757)	32.78(32600)
C_6H_5CO–	17.82(472)	30.90(32100)
p-$CH_3C_6H_4CO$–	17.73(429)	30.82(29900)

Table 3. Electrochemical data for the substituted derivatives $[Cu(Me_2E_2[14]tetraenatoN_4)]$

Substituent(E)	Red / V	Ox ΔEp$_{1/2}$ / V	Red ΔEp$_{1/2}$ / V	ΔEp / mV	Ox ΔEp$_{1/2}$ / V	Red ΔEp$_{1/2}$ / V	ΔEp / mV
CH_3CO-	−1.07	−0.22	−0.15	70	0.84	0.88	40
C_2H_5CO-	−0.95	−0.06	−0.02	40	0.98	1.03	50
i-C_3H_7CO-	−0.82	−0.15	−0.09	60	0.89	0.94	50
p-$NO_2C_6H_4CO-$	−0.98	−0.05	0.01	60	0.95	1.01	60
C_6H_5CO-	−0.88	−0.07	−0.02	50	0.91	0.95	40
p-$CH_3C_6H_4CO-$	−0.85	−0.23	−0.18	50	0.73	0.77	40

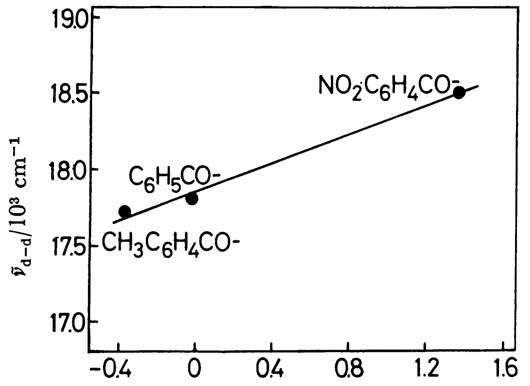

Fig. 3. Plot of d-d transitions energy of the substituted benzoyl derivatives *vs.* Hammett substituent constants of the p-substituent groups.

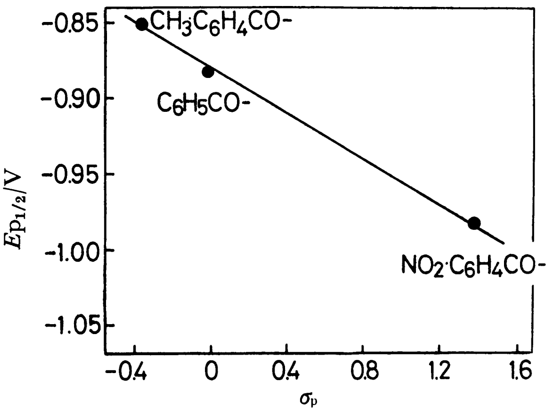

Fig. 4. Plot of reduction potentials of the substituted benzoyl derivatives *vs.* Hammett substituent constants of the p-substituent groups.

overall planarity between the charge-delocalized chelate ring and the substituted π-electron system of the benzoyl group. For the complexes with substituent groups CH_3CO-, C_2H_5CO-, and i-C_3H_7CO-, the tendency of their d-d transition band maxima is observed but not so large.

Electrochemistry. Electrochemical measurements were performed on 10^{-3} mol dm^{-3} solutions of the substituted complexes in acetonitrile. For the direct comparison of the values obtained, the conditions were kept as constant as possible with all the complexes. The cyclic voltamograms of these complexes were similar in shape and showed three electrode processes: (1) the irreversible reduction at a negative potential around −1 V, (2) the relatively well-behaved reduction at around 0 V, and (3) the relatively well-behaved oxidation at a positive potential around 1 V, as given in Table 3. Since Yokoi and Addison[20)] reported that Cu^{2+}/Cu^+ reduction potentials of square planar copper(II) complexes with imine or amine nitrogen atoms are in the range from −0.7 to −1.5 V, the reduction around −1 V of these complexes can be assigned to $Cu^{2+}+e \rightarrow Cu^+$, although it is irreversible. For the p-substituted benzoyl derivatives, only the reduction potential of the three electrode processes is linearly correlated to the Hammett substituent constants of the p-substituent groups, and the slope is −0.072, as shown in Fig. 4. For the corresponding nickel(II) complexes,[5)] the linear correlation between the Hammett substituent constants and the oxidation potentials due to the Ni^{2+}/Ni^{3+} couple was also observed, the slopes being 0.035, 0.064, and 0.047 for the series of 14-, 15-, and 16-membered complexes, respectively.

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References

1) K. M. Kadish and M. M. Morrison, *J. Am. Chem. Soc.*, **98**, 3326 (1976).

2) K. M. Kadish and M. M. Morrison, *Inorg. Chem.*, **15**, 980 (1976).

3) F. A. Walker, D. Beroiz and K. M. Kadish, *J. Am. Chem. Soc.*, **98**, 3484 (1976).

4) D. G. Pillsbury and D. H. Busch, *J. Am. Chem. Soc.*, **98**, 7836 (1976).

5) J. A. Streeky, D. G. Pillsburry, and D. H. Busch, *Inorg. Chem.*, **19**, 3148 (1980).

6) V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 3397 (1972).

7) J. C. Dabrowiak, P. H. Merrell, and D. H. Busch, *Inorg. Chem.*, **11**, 1979 (1972).

8) E. Jäger, *Z. Anorg. Allg. Chem.*, **436**, 76 (1966).

9) D. P. Riley and D. H. Busch, *Inorg. Synth.*, **18**, 36 (1978).

10) H. Okawa and D. H. Busch, *Inorg. Chem.*, **18**, 1555 (1979).

11) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

12) T. Sakurai, H. Iwasaki, Y. Watanabe, K. Kobayashi, Y. Bando, and Y. Nakamichi, *Rep. Inst. Phys. Chem. Res.*, **50**, 75 (1972).

13) C. K. Johnson, Report No. 3794, Oak Ridge National

Laboratory, Oak Ridge, Tennessee (1965).

14) S. Kawano, *Rep. Comp. Cent. Kyushu University*, **13**, 39 (1980).

15) C. H. Wei, *Inorg. Chem.*, **11**, 2315 (1972).

16) R. G. Mirongiu, E. C. Lingafelter, and P. Paoletti, *Inorg. Chem.*, **8**, 2763 (1969).

17) D. Bruins and D. L. Weaver, *Inorg. Chem.*, **9**, 130 (1970).

18) C. J. Hipp, P. W. R. Corfield, J. D. Mokren, and D. H. Busch, *J. Am. Chem. Soc.*, **95**, 4465 (1973).

19) W. P. Schammel, K. B. Mertes, G. G. Christoph, and D. H. Busch, *J. Am. Chem. Soc.*, **101**, 1622 (1979); J. C. Stevens, P. J. Jackson, W. P. Schammel, G. G. Christoph, and D. H. Busch, *ibid.*, **102**, 3283 (1980).

20) H. Yokoi and A. W. Addison, *Inorg. Chem.*, **16**, 1341 (1977).