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Reaction of Dimeric Copper(II) Acetate with Pyridine and Quinoline Bases in Dioxane

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Copper(II) acetate reacts with pyridine and quinoline bases in dioxane giving rise to adduct compounds, which were characterized by UV and EPR techniques. The reaction is formulated as follows:

$$Cu_2(OAc)_4 + L \overset{K_{21}}{\rightleftharpoons} Cu_2(OAc)_4L,$$

where L denotes a free base and K_{21} is an adduct formation constant. Values of K_{21} range from 12 for quinoline or 2-picoline to 146 $mol^{-1}\,dm^{-3}$ for 4-ethylpyridine. A linear free energy relationship is observed between the adduct formation and the protonation of bases in water except for sterically crowded bases.

Considerable interest has been shown in synthesis and physical properties of copper(II) carboxylates and of their adduct compounds with Lewis bases.[1-3] Usually copper(II) carboxylates and their adducts with pyridine bases have absorption maxima at about 370 nm, and the effective magnetic moments of these compounds are less than the spin-only value at room temperature. This has been taken as an indication of a dimeric structure, which is well established by X-ray diffraction studies for copper(II) acetate monohydrate[4] and its pyridine adducts in a solid state.[5]

Copper(II) carboxylate retains the dimeric structure also in solvents with weak solvating power and low dielectric constant, such as ethanol,[6,7] dioxane,[7,8] acetic acid,[9] benzene,[8,10] and chloroform.[10] On the other hand it dissociates into monomers in strongly solvating solvents such as water and pyridine. The latter solvent, having strong coordinating ability, breaks the dimeric structure despite a rather low dielectric constant ($\varepsilon=12$). At any rate dielectric properties may play an important role in the dissociation of the dimer.[11] Few quantitative investigations have, however, been carried out on reactions of these compounds in solution,[10-12] as compared with a number of works on their physical properties in a solid state.[1-3]

In this paper we report the reaction of copper(II) acetate with pyridine and quinoline bases in dioxane ($\varepsilon=2.2$).

Experimental

Reagents. *Dioxane*: Anhydrous tin(II) chloride was added to dioxane (G. R., Wako Pure Chemical Ind. Ltd.) to remove peroxides and the solution was distilled after refluxing for about 10 h. The distillate was then refluxed over sodium for about 10 h, followed by distillation. The water content of the dioxane thus purified was found to be 3.2×10^{-3} to 2.1×10^{-2} M†† by the Karl-Fischer method.

Copper(II) Acetate Solution in Dioxane: G. R. anhydrous copper(II) acetate (Wako Pure Chemical Ind. Ltd.) was washed with dioxane several times before use. The solution was standardized complexiметrically with 4-(2-thiazolylazo)-resorcinol as an indicator.[13]

Pyridine and Quinoline Bases: All bases were distilled under atmospheric or reduced pressure over sodium or potassium hydroxide.

Measurements. All measurements were made at 25±1 °C unless otherwise noted.

Absorbance was measured on a Union Giken spectrophotometer Model SM-401 (absorption curve) or on a Carl Zeiss spectrophotometer Model PMQ II (at 650 nm).

Electron paramagnetic resonance spectra were obtained with a JEOL ES-SCXA X-band spectrometer.

Results and Discussion

An apparent molar extinction coefficient remained constant at 650 nm for a solution containing copper(II) acetate alone over the concentration range from 3.7×10^{-4} to 4.6×10^{-3} M ($\varepsilon_0=220\pm5$ $M^{-1}\,cm^{-1}$†††). This indicates retention of the dimeric structure. Absorption spectra are shown in Fig. 1 for a copper(II) acetate–pyridine system, and similar ones are observed for the other bases employed. Addition of a base gives rise to a considerable change in absorption in the visible region, in contrast to virtual invariance of the shoulder discernible at about 370 nm. Since all the bases used in the present study do not absorb in these regions, this spectral behavior may be accounted for by coordination of the base to an apical position of a copper(II) dimer without dissociation into monomers.[10]

This argument is substantiated by the fact that the red shift of the band I in solution corresponds well to that in a solid state on addition of pyridine,[8] which is summarized in Table 1.

Presence of isosbestic points in Fig. 1 suggests only

Table 1. Absorption maxima of pyridine adducts

species[a]	Band I[b]	Band II[b]	State	Ref.
$Cu_2(OAc)_4$	682	370	Solid[c]	d)
$Cu_2(OAc)_4L$	718	370	Solid[c]	d)
$Cu_2(OAc)_4L$	680	370	Solid[e]	f)
$Cu_2(OAc)_4$	662	373	In dioxane	d)
$Cu_2(OAc)_4$	665	370	In dioxane	g)
$Cu_2(OAc)_4L$	708	375	In dioxane	d)

a) L represents pyridine. b) The wavelength expressed in nm. c) Nujol mull. d) The present work. e) Reflectance spectra. f) 8b. g) 8a.

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†† Throughout this paper: 1 M=1 mol dm^{-3}.

††† Extinction coefficients and molarities are both based on formula weights.

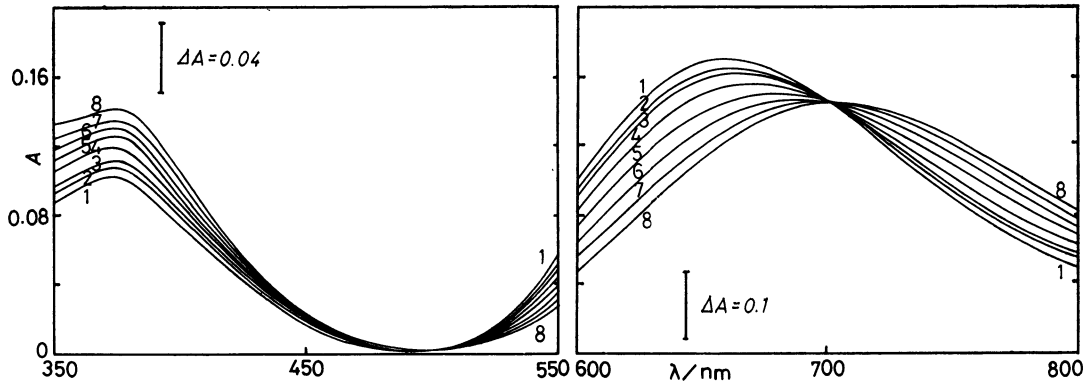

Fig. 1. Absorption spectra of the solutions of copper(II) acetate and pyridine.
$C_{Cu}=1.993\times10^{-3}$ M. $C_L/C_{Cu}=(1)$ 0, (2) 0.614, (3) 2.47, (4) 6.16, (5) 8.65, (6) 10.5, (7) 14.8, (8) 24.7.
The figure at right is diminished in scale on the abscissa by a factor of 2.5.

one chemical equilibrium between a base and the dimeric acetate. Therefore the main reaction may be formulated as follows:

$$Cu_2(OAc)_4 + nL \overset{K_{2n}}{\rightleftharpoons} Cu_2(OAc)_4L_n, \quad (1)$$

where L denotes a free base and K_{2n} is the constant for the equilibrium (1). Unless the base concentration is considerably high, a 1 : 1 complex will predominate ($n=1$). Let D and DL stand for $Cu_2(OAc)_4$ and $Cu_2(OAc)_4L$ respectively, then consideration of stoichiometric relations gives the following expressions:

$$A = 2\varepsilon_0[D] + 2\varepsilon_{21}[DL] \quad (2)$$

$$A_0 = \varepsilon_0 C_{Cu} \quad (3)$$

$$C_{Cu} = 2[D] + 2[DL] \quad (4)$$

$$C_L = [L] + [DL], \quad (5)$$

where A and A_0 are the absorbances at 650 nm in the presence and in the absence of a base, ε_0 and ε_{21} the molar extinction coefficients of D and DL. C_{Cu} and C_L represent the total concentrations of copper and a base, respectively.

Combination of these equations leads to:

$$\frac{C_{Cu}C_L}{A-A_0} = \frac{1}{\varepsilon_{21}-\varepsilon_0}\left[C_L+\frac{C_M}{2}-\frac{A-A_0}{2(\varepsilon_{21}-\varepsilon_0)}\right] + \frac{1}{K_{21}(\varepsilon_{21}-\varepsilon_0)}. \quad (6)$$

Plots of the left-hand side against $[C_L+C_M/2-(A-A_0)/2(\varepsilon_{21}-\varepsilon_0)]$ yielded a family of straight lines as was expected, with ε_{21} roughly chosen. A better extinction coefficient ε_{21} and an adduct formation constant K_{21} were obtained from the gradient and the intercept of the straight line (Fig. 2).

Formation of the 1 : 1 adduct DL was confirmed in a more general fashion.

An apparent molar extinction coefficient may be expressed in the following way:

$$\varepsilon = \frac{A}{C_M} = \frac{\varepsilon_0+\varepsilon_{2n}K_{2n}[L]^n}{1+K_{2n}[L]^n}. \quad (7)$$

Transformation of Eq. 7 gives

$$\log(\varepsilon_0-\varepsilon) = \log(\varepsilon_0-\varepsilon_{2n}) + \log\left(\frac{K_{2n}[L]^n}{1+K_{2n}[L]^n}\right). \quad (8)$$

A plot of $\log(\varepsilon_0-\varepsilon)$ against $\log[L]$ may be compared with a family of normalized curves with different parameter n, that is $y=\log[p^n/(1+p^n)]$ as a function of $x=\log p$. As is evident from Fig. 3, the best fit curve is obtained when $n=1$, and the values of ε_{21} and K_{21} were

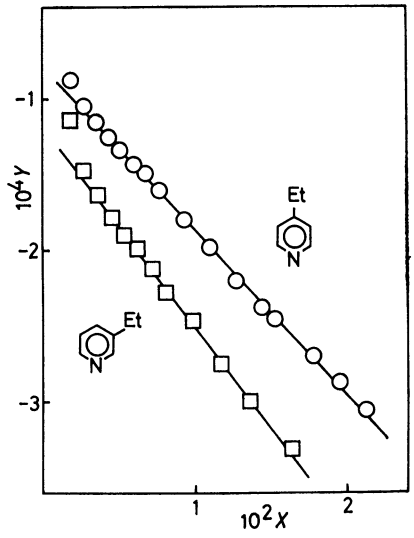

Fig. 2. Linear plot for change in absorbance at 650 nm.
$y=C_{Cu}C_L/(A-A_0)$, $x=C_L+C_M/2-(A-A_0)/2(\varepsilon_{21}-\varepsilon_0)$.
See Eq. 6.
○: 4-Ethylpyridine, $C_{Cu}=2.44_7\times10^{-3}$ M, □: 3-ethylpyridine, $C_{Cu}=2.14_8\times10^{-3}$ M.

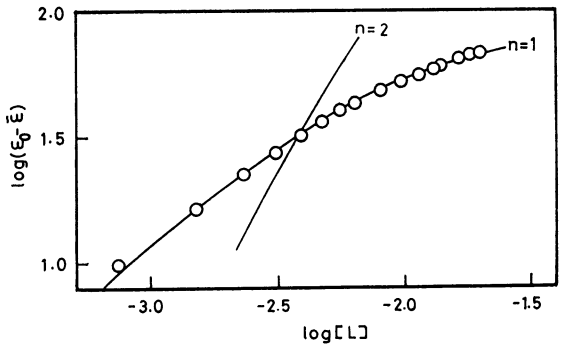

Fig. 3. Curve-fitting of change in absorbance at 650 nm for 4-ethylpyridine (Eq. 9).
[L] was refined with the computer and $C_{Cu}=2.44_7\times10^{-3}$ M.

TABLE 2. ADDUCT FORMATION CONSTANTS

Base	K_{21}/M^{-1}	$\varepsilon_{21}/M^{-1}\,cm^{-1}$ e)	pK_a
Pyridine	83±9	136±5	5.19a)
2-Picoline	12±6	116±3	5.95a)
3-Picoline	98±21	131±4	5.66a)
4-Picoline	114±13	138±4	6.00a)
2,4-Lutidine	25±6	126±4	6.74a)
3,5-Lutidine	132±9	129±4	6.09a)
3,4-Lutidine	137±22	127±3	6.47a)
2,6-Lutidine	f)		6.71a)
3-Ethylpyridine	97±13	139±5	5.70b)
4-Ethylpyridine	146±6	134±4	6.02b)
Collidine	f)		7.59c)
Quinoline	12±1	144±3	4.93d)
Isoquinoline	73±1	135±4	5.46d)

Protonation constants pK_a refer to 25 °C and $\mu=0$ M unless otherwise noted.
a) H.-H. Perkampus and G. Prescher, *Ber. Bunsenges. Phys. Chem.*, **72**, 429 (1968). b) H.C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, **77**, 1723 (1955). c) H. C. Brown, D. Gintis, and H. Podall, *J. Am. Chem. Soc.*, **78**, 5375 (1956). d) A. Albert and J. N. Phillips, *J. Chem. Soc.*, **1956**, 1294. e) At 650 nm. f) Too small to evaluate.

determined by the curve-fitting method.

These values were further refined by the least squares method with an electronic computer FACOM 230-75 at Computation Center of Nagoya University. The final results are summarized in Table 2.

The experimental data were also treated by plotting graphically the spectral change at 650 nm as well as by refining with the computer, dissociation of the dimer being assumed as the main reaction. Then the predominant reaction might be written as follows:

$$Cu_2(OAc)_4 + 2nL \overset{K_{1n}}{\rightleftharpoons} 2Cu(OAc)_2L_n. \qquad (9)$$

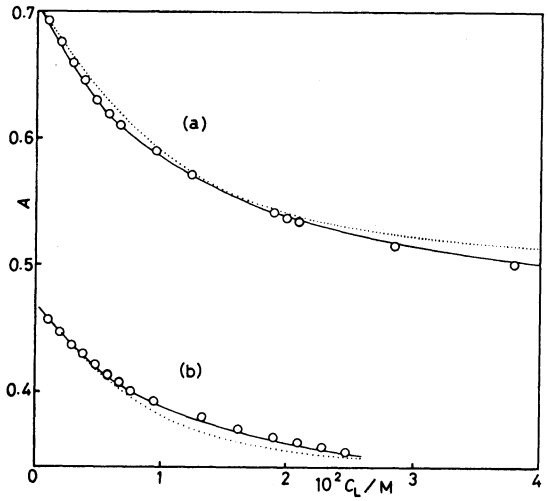

Fig. 4. Change in absorbance at 650 nm with the concentration of 3-ethylpyridine.
a) $C_{Cu}=3.22_1\times10^{-3}$ M. b) $C_{Cu}=2.14_8\times10^{-3}$ M.
○ refers to the experimental value. ——: Calculated curve assuming DL alone, ……: calculated curve assuming ML alone. It was drawn with tentative values of $K'_{11}=78.8\ M^{-1}$ and $\varepsilon'_{11}=156\ M^{-1}\,cm^{-1}$ (see text).

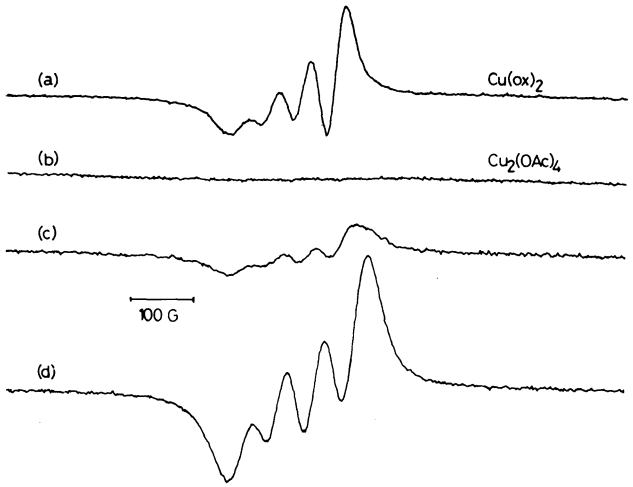

Fig. 5. EPR spectra of dioxane solutions at room temperature (about 20 °C).
a): Copper(II) 8-quinolinolate ($C_{Cu}=6.10\times10^{-5}$ M), b): $C_{py}=0$ M, c): $C_{py}=2.62\times10^{-2}$ M, d) $C_{py}=2.47_2\times10^{-1}$ M.
The concentration was $2.39_2\times10^{-3}$ M in copper(II) acetate except for a).

The assumption of a monomer formation alone results in a systematic deviation of the calculated curves from the experimental data for 3-ethylpyridine as shown in Fig. 4. The dotted lines are drawn with tentative values of K'_{11} and ε'_{11}[14] that gave the best fit to the data on assuming only the Eq. 9. In the case of pyridine, however, the dissociation reaction also accounts for the spectral change satisfactorily when $n=1$.

This finding prompted us to an electron paramagnetic resonance study. A solution containing copper(II) acetate alone did not exhibit any EPR spectra other than ones characteristic of the dimeric structure, while typical copper(II) spectra began to appear on addition of pyridine at concentrations higher than those used in the UV study (Fig. 5). Analysis of spin concentration was carried out for a monomeric form by double integration of the spectra.[15] Copper(II) 8-quinolinolate in dioxane was selected as a standard, since the shape of EPR spectra is similar to those of monomeric copper(II) acetate. Table 3 indicates that the monomeric concentration [ML] thus determined experimentally is much lower than the value of [ML]', which was tentatively estimated with $K'_{11}=11.3\ M^{-1}$ (*cf.* Eq. 9).

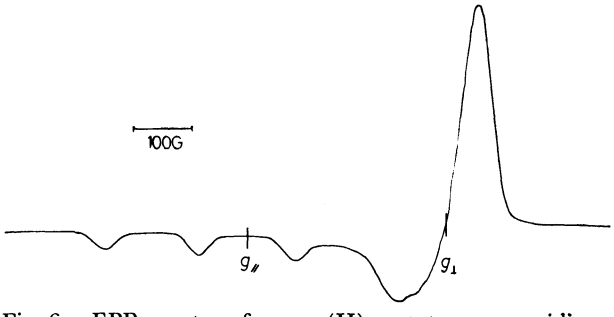

Fig. 6. EPR spectra of copper(II) acetate monopyridine adduct in dioxane at 99.3 K.
$C_{py}=2.47_2\times10^{-1}$ M and $C_{Cu}=2\times10^{-3}$ M.

TABLE 3. COMPARISON OF MONOMERIC AND DIMERIC SPECIES [a)]

No.	10 C_L/M	10^3[ML]′/M[b)]	10^4[ML]/M	10^3[DL]/M	[L]/M	log (K_{11}/M^{-1})
1	0.131	1.05	0.24	0.609	0.0125	−2.20
2	0.262	1.62	0.35	0.811	0.0254	−2.31
3	0.524	2.09	0.71	0.969	0.0514	−2.08
4	0.786	2.24	1.00	1.035	0.0775	−1.99
5	1.236	2.33	1.13	1.089	0.1225	−2.10
6	2.472	2.38	1.69	1.140	0.2461	−2.07

a) L, ML, and DL denote pyridine, $Cu(OAc)_2L$, and $Cu_2(OAc)_4L$, respectively. The concentration of copper(II) acetate was maintained at $2.39_2 \times 10^{-3}$ M. b) [ML]′ was calculated using a tentative value of K'_{22}= 11.3 M^{-1} (see text).

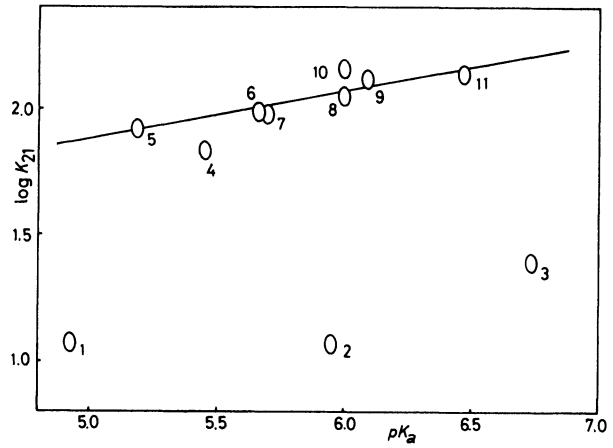

Fig. 7. Linear free energy relationship between the addition of bases to dimeric copper acetate and the protonation of bases.
1): Quinoline, 2): 2-picoline, 3): 2,4-lutidine, 4): isoquinoline, 5): pyridine, 6): 3-picoline, 7): 3-ethylpyridine, 8): 4-picoline, 9): 3,5-lutidine, 10): 4-ethylpyridine, 11): 3,4-lutidine.

In brief, monomeric species appear appreciably only when a base concentration becomes much higher. The last column in Table 3 shows experimental quotients $K_{11}=[ML]^2/[D][L]^2$, which are roughly constant (log $K_{11}=-2.1\pm0.1$).

The EPR spectra at room temperature (about 20 °C) gave merely an average value of g, which was determined as $\bar{g}=2.142$ from Fig. 5. Therefore spectra were also measured at 99.3 K for a dioxane solution, and $g_\perp=2.063$ and $g_{//}=2.309$ were obtained (Fig. 6). These values give $g=2.148$ in a fair accord with the above value found at room temperature, and are compared with the values $g_x=2.065$, $g_y=2.070$, and $g_z=2.362$ for the crystal of $Cu_2(OAc)_4Py_2$.[16] Distortion from the O_h symmetry with an elongation along the z axis is expected in the monomeric $Cu(OAc)_2Py$, because $g_{//}>g_\perp>2$.[17]

For most bases the formation constant of the 1 : 1 adduct log K_{21} increases linearly with pK_a of a base as illustrated in Fig. 7. Among the pyridine bases examined, however, 2-picoline and 2,4-lutidine have abnormally low formation constants, possibly because of the steric hindrance of 2-methyl group. More crowded 2,6-lutidine and collidine hardly react with copper(II) acetate. The steric effect of an adjacent benzene ring is also observed with quinoline.

Similar relations are also observed in other systems, such as copper(II)–β-diketone,[18–20] oxovanadium(IV)–β-diketone,[21] and 2,3-butanedionebis(benzoylhydrazonato)nickel(II)[22] complexes with pyridine or quinoline bases. A linear free energy relationship is also found between the adduct formation constant for copper(II) acetate (log K_{21}) and that for bis(acetylacetonato)oxovanadium(IV) (log K_x) with pyridine or quinoline bases. Linearity holds, however, for all bases including the sterically crowded ones, as shown in Fig. 8.

Contrary to exclusive formation of a 1 : 2 adduct DL_2 in a solid state, a 1 : 1 species DL predominates in

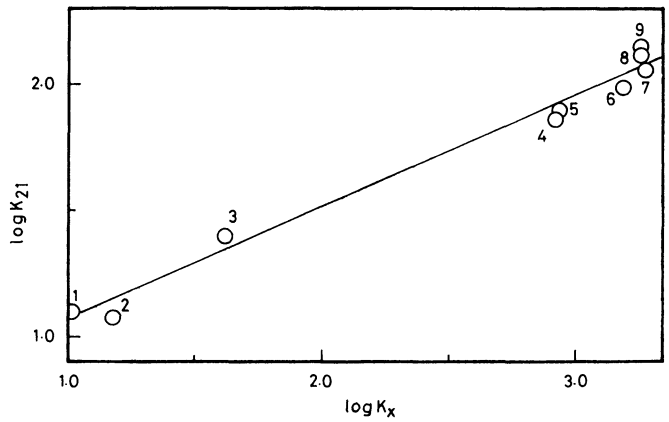

Fig. 8. Linear free energy relationship for the addition reactions of bases.
K_{21} refers to dimeric copper(II) acetate and K_x to bis(acetylacetonato)oxovanadium(IV).
1): 2-Picoline, 2): quinoline, 3): 2,4-lutidine, 4): isoquinoline, 5): pyridine, 6): 3-picoline, 7): 4-picoline, 8): 3,5-lutidine, 9): 4-ethylpyridine.

dioxane. This is rather unusual when compared with the reactions in other solvents. In anhydrous acetic acid, for example, copper acetate dissociates into monomer at early stage on addition of lithium acetate[9] and pyridine,[23] with rapid dissappearance of the shoulder at 370 nm. Extraction of copper(II) with an aliphatic long chain carboxylic acid also revealed existence of a monomer ML as well as a dimer DL in the presence of pyridine in benzene.[12]

Adduct formation may be interpreted in terms of substitution of a solvent molecule, bound to an apical site of the dimeric copper(II), by a base which has stronger coordination power than dioxane.

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References

1) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

2) J. Catterick and P. Thornton, "Structures and Physical Properties of Polynuclear Carboxylates," in "Advances in Inorganic Chemistry and Radiochemistry," ed by H. J. Emeléus and A. G. Sharpe, Academic Press (1977), Vol. 20, pp. 291—362.

3) R. J. Doedens, "Structure and Metal-Metal Interactions in Copper(II) Carboxylate Complexes," in "Progress in Inorganic Chemistry," ed by S. J. Lippard, John Wiley & Sons, New York (1976), Vol. 21, pp. 209—231.

4) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1953).

5) a) G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, **1961**, 5244; b) F. Hanic, D. Štempelová, and K. Hanicová, *Acta Crystallogr.*, **17**, 633 (1964).

6) S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **30**, 953 (1957).

7) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 468 (1958).

8) a) R. L. Martin and A. Whitley, *J. Chem. Soc.*. **1958**, 1394; b) L. Dubicki and R. L. Martin, *Inorg. Chem.*, **5**, 2203 (1966).

9) K. Sawada, H. Ohtaki, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **34**, 625 (1972).

10) D. P. Graddon, *J. Inorg. Nucl. Chem.*, **17**, 222 (1961).

11) H. Grasdalen and I. Svare, *Acta Chem. Scand.*, **25**, 1089 (1971); H. Grasdalen, *ibid.*, **25**, 1103 (1971).

12) K. Hirose, N. Matsumoto, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **39**, 2261 (1977).

13) H. Wada and G. Nakagawa, *Jpn. Analyst*, **14**, 28 (1965).

14) The prime was affixed to emphasize a hypothetical nature of the reaction (9).

15) R. S. Alger, "Electron Paramagnetic Resonance," Interscience, New York (1968). (Translation into Japanese by T. Isobe *et al.* Yoshioka-shoten (1973), p. 224).

16) F. E. Mabbs, J. K. Porter, and W. R. Smail, *J. Inorg. Nucl. Chem.*, **36**, 819 (1974).

17) B. A. Goodman and J. B. Raynor, "Electron Spin Resonance of Transition Metal Complexes," in "Advances in Inorganic Chemistry and Radiochemistry," ed by H. J. Emeléus and A. G. Sharpe, Academic Press (1970), Vol. 13, pp. 135—362.

18) T. Shigematsu, M. Tabushi, M. Matsui, and M. Munakata, *Bull. Chem. Soc. Jpn.*, **41**, 2656 (1968); T. Shigematsu, M. Matsui, Y. Sasaki, and M. Sakurada, *ibid.*, **49**, 2325 (1976); Y. Sasaki, M. Sakurada, M. Matsui, and T. Shigematsu, *ibid.*, **52**, 2295 (1979).

19) D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).

20) K. Ueda, *Bull. Chem. Soc. Jpn.*, **51**, 805 (1978).

21) E. Kwiatkowski and J. Trojanowski, *J. Inorg. Nucl. Chem.*, **38**, 131 (1976).

22) L. Sacconi, G. Lombardo, and P. Paoletti, *J. Inorg. Nucl. Chem.*, **8**, 217 (1958).

23) K. Hasegawa, unpublished results.