Transition-metal Complexes of Pyrrole Pigments. III. Copper(II) and Zinc(II) Complexes of 1,19-Dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac[1]

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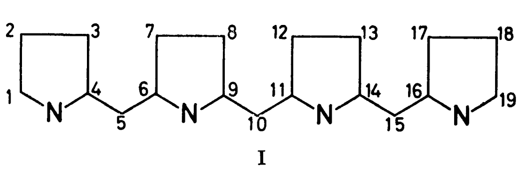
The copper(II) and zinc(II) complexes of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac were synthesized and investigated by near-ultraviolet, visible, near-infrared, infrared, NMR, and ESR measurements as well as X-ray diffraction measurements of powdered samples. The ligand-field bands appeared at 701 and 752 mμ for the copper complex provided information on its geometry around the central metal atom. Namely, the copper atom is subjected to the square-planar ligand-field in the complex. Infrared bands characteristic of asymmetric stretching vibration of the carbethoxy groups at 8 and 12, and X-ray powder diffraction pattern gave another support to this structure by referring to the corresponding data for the nickel complex. ESR measurements also provided the spin Hamiltonian parameters consistent with the square-planar coordination. The most plausible structure for the zinc complex was concluded to be the binuclear form with tetrahedral coordination in conformity with that for the cobalt complex, which was revised in this work. Infrared bands in the 1100—1300 cm^{-1} range due to asymmetric vibration of the ester groups at 8 and 12, and X-ray powder pattern provided the evidence for this structure in reference to the corresponding data for the cobalt complex. The up-field shift of proton signals due to the methyl groups at 1, 7, 13, and 19, the 10-methylene group, and to the ethyl moiety of carbethoxy groups at 8 and 12 upon coordination are consistent with the tetrahedral coordination with dimeric structure. The molecular weight determination also confirmed the dimeric nature of the zinc complex.

Bilirubin and mesobilirubin are the typical biochemical compounds possessing a saturated methylene bridge at the center of a linear tetrapyrrolic structure, each of the four pyrrole rings of which are linked by a single carbon atom. These biladienes-ac are the members of so called bile pigments and have been extensively studied from biochemical point of view. Meanwhile, these biladienes (I) in general may behave as tetradentate ligands and produce various complex metal chelate compounds. In our previous work,[2] the cobalt and nickel complexes of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac (II) were synthesized and investigated by means of various spectroscopic methods. As a result, a dimeric structure was assigned to the cobalt complex in which each cobalt atom attained approximately a tetrahedral configuration (III). On the other hand, the nickel atom was found to be subjected to the square-planar ligand-field in the complex of monomeric type (IV).



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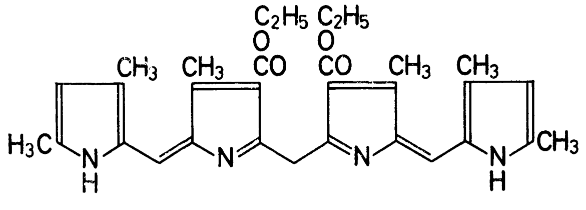

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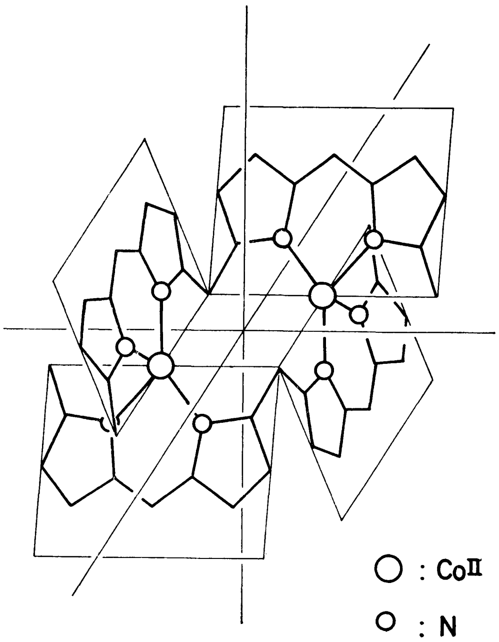

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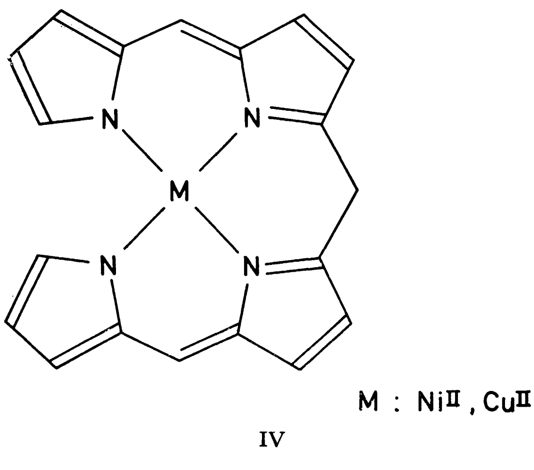

IV

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[1] Contribution No. 196 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

[2] Y. Murakami, Y. Kohno, and Y. Matsuda, *Inorg. Chem. Acta*, **3**, 671 (1969).

This paper reports the synthesis and the structural properties of copper(II) and zinc(II) complexes of the above biladiene pigment, as examined by visible, near-infrared, infrared, NMR, and ESR measurements as well as X-ray diffraction measurements of powdered samples. Since copper and zinc tend to assume square-planar and tetrahedral configurations, respectively, coordination configurations of the present metal complexes are to be discussed in reference to the corresponding nickel and cobalt complexes already reported.[2]

Experimental

Spectral Measurements. Visible and near-infrared spectra in chloroform (10^{-3}—10^{-5} M) were recorded on a Hitachi Model EPS-2 spectrophotometer at room temperature. Infrared and far-infrared spectra covering the range 4000—200 cm^{-1} were measured with a JASCO Model DS-403G grating spectrophotometer at room temperature, where both KBr disc and Nujol mull techniques were adopted. A Varian A-60 spectrometer was used to obtain NMR spectra in chloroform-d (3×10^{-2} M) at room temperature. Chemical shifts were reported in ppm from internal tetramethylsilane (TMS) and calibrated by the use of chloroform signal as the secondary reference. ESR spectra were taken on a JEOL JES-ME-3X X-band spectrometer using 100 kHz field modulation, where the copper-doped crystals (~1 wt%) of the isomorphous nickel complex and the xylene-benzene solution of the copper complex at room temperature as well as the frozen sample of the copper complex in xylene-benzene at 77°K were used as samples. X-Ray diffraction patterns of the powdered solid samples were measured with a Norelco X-ray diffractometer.

Zinc Complex. A 300 mg sample of zinc acetate dihydratein 10 m*l* of methanol was added to a suspension of 300 mg of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac[2] (abbreviated as BLD hereafter) (free base) and 400 mg of sodium acetate trihydrate in 50 m*l* of methanol while heating on a water-bath. After refluxing for one hour, the mixture was allowed to cool down to room temperature. Reddish violet crystals were recovered and recrystallized from acetone: yield 250 mg (74.4%). Further recrystallization was performed from chloroform-methanol: 200 mg; mp>250°C(decomp.).

Found: C, 62.88; H, 5.93; N, 9.29%;[3] mol wt (osmometric method[4]), 1230. Calcd for $C_{62}H_{68}N_8O_8Zn_2$: C, 62.89; H, 5.79; N, 9.46%; mol wt, 1184.05.

Copper Compex. A 500 mg sample of copper acetate monohydrate in 30 m*l* of methanol was added to a mixture of 300 mg of the free base of BLD, 600 mg of sodium acetate trihydrate and 120 m*l* of methanol, and refluxed for 40 min. The dark crystalline precipitate was recovered and washed several times with methanol. The chloroform solution of this material was applied to the top of a chromatographic column of silica gel (60—80 mesh, Kanto Chemical Co., Inc.) and eluted with chloroform. The initial effluent was concentrated *in vacuo* and the product was recovered by reprecipitation with methanol: dark crystalline solid of metallic luster; yield 150 mg (44.3%). Further recrystallization was performed from chloroform-methanol: 120 mg; mp 214—217°C (decomp.).

Found: C, 62.76; H, 5.84; N, 9.35%; mol wt (osmometric method), 603. Calcd for $C_{31}H_{34}N_4O_4Cu$: C, 63.09; H, 5.81; N, 9.49%; mol wt, 590.18.

Results and Discussion

Electronic Spectra. The near-ultraviolet, visible, and near-infrared spectra for the BLD free base and the corresponding zinc and copper complexes in chloroform are shown in Fig. 1. The biladiene shows two intense absorption bands at 425 and 495 mμ, whose absorption coefficients are 27700 and 14800 respectively. These are attributed to the $\pi\rightarrow\pi^*$ transition.[5] Other broad bands located in the near-ultraviolet region may be due to the transitions to higher π energy levels.

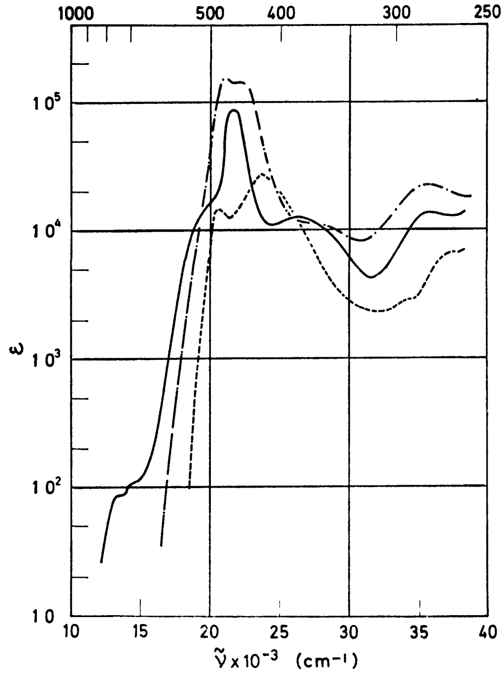

Fig. 1. Electronic absorption spectra in chloroform: ——, BLD free base; —·—·—, the zinc complex; – – –, the copper complex.

The zinc complex shows four absorption bands in the 260—1000 mμ range. The bands in a higher energy region—282 mμ (ε=22800) and 356 mμ (ε=11400)—are considered to be due to the $\pi\rightarrow\pi^*$ transitions for which the ligand part is responsible. Both of the quite intense bands appearing at 454 mμ (ε=146000) and 475 mμ (ε=153000) are tentatively assigned to the metal to ligand charge transfer transitions, judging from their intensity and location. In the longer wavelength region beyond 620 mμ, there observed no significant absorption bands whose intensity is higher than 0.1.

The copper complex demonstrates six absorption bands in the 260—1000 mμ range, among which the

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3) The elemental analyses were performed at the Microanalysis Center of Kyushu University.

4) A Hitachi Model 115 vapor pressure osmometer was used to measure the molecular weight of a sample dissolved in chloroform.

5) The spectrum of the BLD free base has been shown in our previous paper.[2] Its absorption intensity indicated in Fig. 1 of the previous paper is twice as large as the real value as a matter of fact. The correction has to be made for this mis-presentation of the spectrum.

higher energy bands observed at 280 mμ (ε=13700) and 380 mμ (ε=12700) are attributed to the $\pi \to \pi^*$ transitions of the ligand part. The most intense band appearing at 461 mμ (ε=97800) is assignable to the metal to ligand charge transfer transition, while the weaker bands at 701 mμ (ε=103) and 752 mμ (ε=85) in a lower energy region of the present study is due to the $d \to d$ transitions of the metal atom. When the copper atom is placed in the square-planar ligand-field, a $d \to d$ $(d_{z^2}, d_{xy}, d_{xz}, d_{yz} \to d_{x^2-y^2})$ absorption band has been known to appear in the 500—700 mμ range. In the case that the copper ion is subjected to a strong ligand-field perturbation produced by the four nitrogen donor atoms, such a $d \to d$ band can be found in general near the 500 mμ range.[6] The corresponding absorption intensity varies from several tens to a few hundreds, depending upon the structure of the ligand part.[7] When the copper complex assumes approximately a tetrahedral configuration around the central metal atom, no significant absorption bands originated from $d \to d$ transitions are seen in a shorter wavelength region lying below 1000 mμ.[8] If the coordination configuration is something between these two typical cases or the symmetry property of the ligand-field is lowered below D_{4h}, the multi-absorption bands tend to appear in the intermediate wavelength range with significant energy separation.[9,10] The above consideration leads to the conclusion that the copper atom in the BLD complex attains primarily the square-planar coordination without much distortion.

Vibrational Spectra. The infrared spectra in the 1000—1600 cm^{-1} range for the BLD free base and its zinc and copper complexes are shown along with those for the corresponding cobalt and nickel complexes in Fig. 2. The vibrational character of a family of tetrahedral complexes is found to be different from that of square-planar complexes particularly in the 1100—1300 cm^{-1} range in the present study. These characteristic bands are attributed to the asymmetric stretching modes of the ester group situated at positions 8 and 12 in the ligand part.[11]

The cobalt complex, where the metal atom has been shown to assume a tetrahedral coordination,[2] shows two absorption bands of equal intensity and a shoulder band in between in this range as shown in Fig. 2 by arrows. The present zinc complex demonstrates vibrational characteristics quite similar to those of the corresponding cobalt complex.

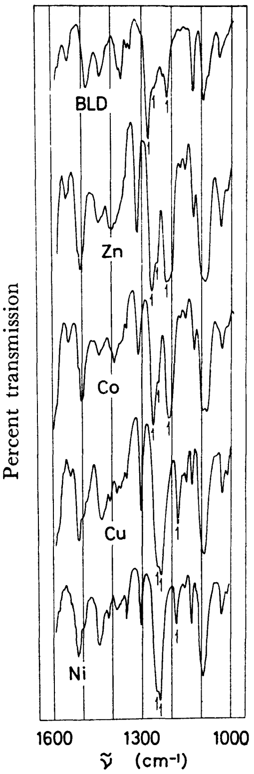

Fig. 2. Infrared spectra of the BLD complexes of bivalent metals (KBr disc method). Arrows refer to the characteristic bands due to asymmetric stretching vibration of the carbethoxy group (see text).

On the other hand, two strong bands of nearly equal intensity are located closely in the higher frequency part of the 1100—1300 cm^{-1} range and another band of medium intensity is found in the lower frequency part for the nickel complex which assumes a square planar configuration around the metal atom, as seen in Fig. 2. The present copper complex also shows vibrational bands of similar trend in the same frequency range. The infrared spectrum of the BLD free base appears to bear a resemblance to those of the cobalt and zinc complexes rather than those of the corresponding copper and nickel complexes. Outside this region some minor differences between these two types of complexes can be noticed around 1400 and 1550 cm^{-1}.

The above results indicate that the carbethoxy groups located at positions 8 and 12 of the ligand part in the cobalt and zinc complexes of tetrahedral configuration

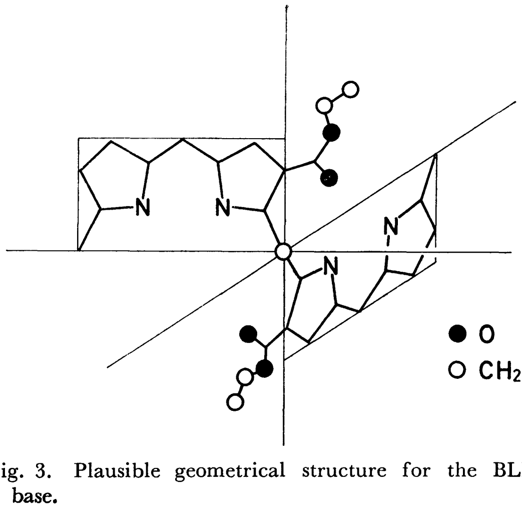

Fig. 3. Plausible geometrical structure for the BLD free base.

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[6] R. E. Clarke and J. H. Weber, *J. Inorg. Nucl. Chem.*, **30**, 1837 (1968).

[7] R. L. Belford and W. A. Yeranos, *Mol. Phys.*, **6**, 121 (1963).

[8] A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier Publishing Co., Amsterdam (1968), p. 359.

[9] M. Goodgame and L. I. B. Haines, *J. Chem. Soc., A*, **1966**, 174.

[10] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 915 (1967).

[11] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York (1964), p, 249.

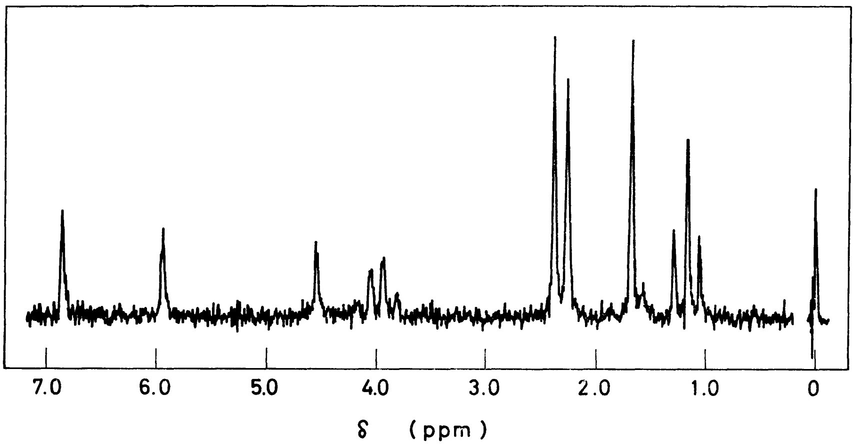
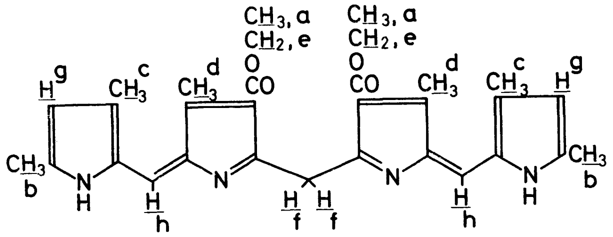


Fig. 4. NMR spectrum of the Zn(II)-BLD complex in chloroform-*d*; TMS as an internal reference.

TABLE 1. PROTON CHEMICAL SHIFTS FOR BLD AND THE METAL COMPLEXES

	Solvent	δ, ppm								Ref.
BLD	CCl_4	1.32	2.08	2.18	2.42	4.26	4.69	5.85	6.65	2
Ni complex	$CDCl_3$	1.39	1.98	2.18	2.57	4.33	4.87	5.93	7.00	2
Zn complex	$CDCl_3$	1.19	1.70	2.25	2.40	4.01	4.55	5.94	6.86	This work
Assignment		a	b	c	d	e	f	g	h	



are free from steric strain as expected in the ligand free base, a plausible structure for which is depicted in Fig. 3.

By inference from the far-infrared study on the dipyrromethene complexes,[12,13] absorption bands due to metal-nitrogen stretching modes are expected to appear in the 300—400 cm^{-1} range. Nevertheless, any reasonable assignments of empirical nature were not possible at present due to the complexity of these spectra caused by vibrational modes of the ligand part.

NMR Spectrum of the Zinc Complex. The NMR spectrum for the zinc complex is shown in Fig. 4 and the assignments are listed in Table 1 together with those for the BLD free base and the corresponding nickel complex. The proton signals due to the 3- and 17-methyl groups, the 2- and 18-protons, and the 5- and 15-methine groups shifted down-field upon coordination with zinc. All other proton signals, on the other hand, shifted up-field. The electron density around methine-carbon atoms at positions 5 and 15 seems to be decreased through delocalization caused by chelate ring formation, and the protons attached to these carbon atoms are deshielded as a result. This electronic effect for the zinc complex is smaller than that for the nickel complex. The similar explanation may be given to other proton signals which demonstrate down-field shift as mentioned above. The signal for protons of the 10-methylene group in the zinc complex is found in the highest field among the corresponding signals for the three compounds listed in Table 1. This is most likely due in part to the fact that the 10-methylene group is not involved in a chelate ring through coordination, while this group becomes a member of the chelate ring in the corresponding nickel complex of square-planar configuration. The similar trend was also observed for the proton signals due to the ethyl moiety of carbethoxy groups at positions 8 and 12, as well as for the signal due to the 7- and 13-methyl groups. Placement of these groups in the shielding zones of near-by pyrrole rings of another BLD molecule and the corresponding chelate rings in the same complex seems to result in such up-field shifts of the corresponding proton signals. This situation can be visualized by Fig. 5, where the zinc atoms are bound to pyrrolic nitrogens by assuming a tetrahedral configuration at a 2 : 2 molar ratio of ligand to metal. The ligand molecule attains a conformation entirely similar to that expected in the free base state

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[12] Y. Murakami and K. Sakata, *Inorg. Chem. Acta*, **2**, 273 (1968).

[13] Y. Murakami, K. Sakata, and Y. Matsuda, unpublished results.

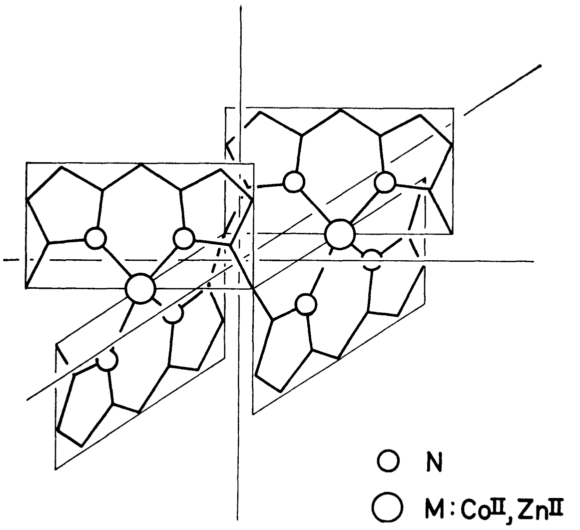

Fig. 5. The most plausible structure for the Co(II)- and Zn(II)-BLD complexes; the binuclear structure with tetrahedral coordination of metal atoms.

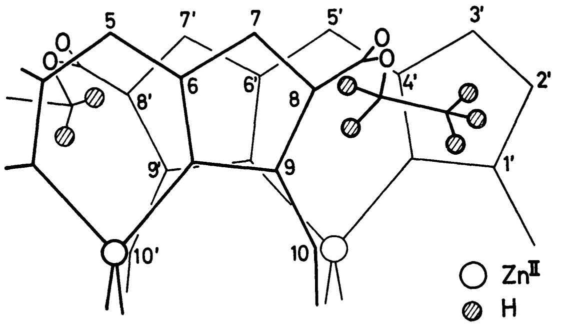

Fig. 6. Plausible geometrical configuration of the 8-carbethoxy group in the Zn(II) complex of binuclear structure.

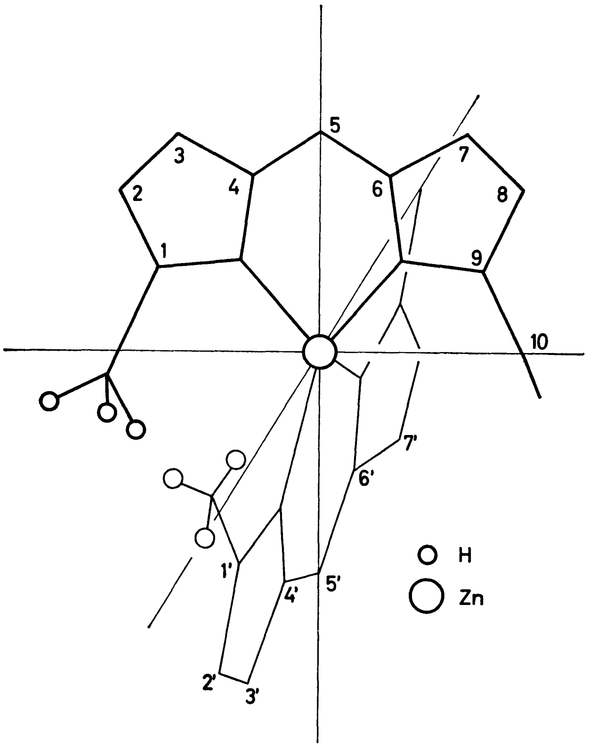

Fig. 7. Plausible geometrical configuration of the 1-methyl group in the Zn(II) complex of binuclear structure.

(Fig. 3) and the least steric interaction between the carbethoxy groups at positions 8 and 12 seems to be secured as a result. The state of affair around the 8- and 12-carbethoxy groups is shown in more understandable manner in Fig. 6. This is in agreement with the conclusion derived from the infrared data. A significant up-field shift of the proton signal due to the 1- and 19-methyl groups may also be caused by the shielding effect of pyrrole rings and metal chelate rings as shown in Fig. 7. The situation would be somewhat different in the nickel complex. A steric interaction between the 1- and 19-methyl groups in the monomeric nickel complex of square-planar coordination seems to result in a slight twist of these groups from the plane of each pyrrole ring. This effect would place these methyl groups in an edge of the shielding zone of each pyrrole ring.

ESR Spectra of the Copper Complex. The ESR spectra for the copper complex in xylene-benzene at room temperature and at 77°K as well as that doped in the isomorphous nickel complex at room temperature are shown in Fig. 8. The general feature of spectra B and C is consistent with the square-planar coordination. In these two spectra, the hyperfine lines due

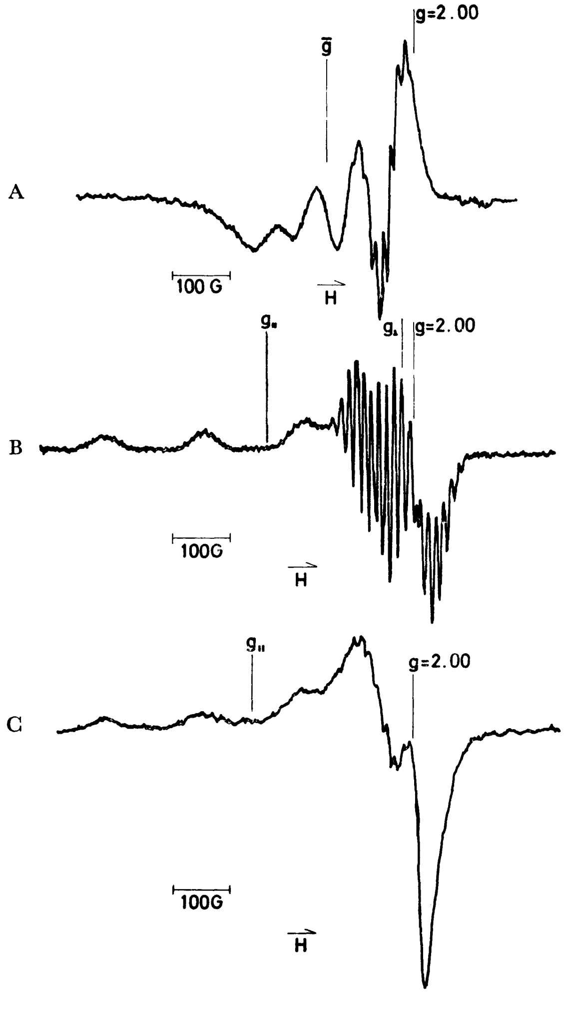

Fig. 8. ESR spectra of the Cu(II)-BLD complex: A, in xylene-benzene (6 : 4) at room temperature; B, in xylene-benzene (6 : 4) at 77°K; C, doped in the Ni(II)-BLD complex at room temperature.

to the copper nucleus can be observed on the $g_{\parallel}$ positions while such splittings are not obvious on the $g_{\perp}$ positions. Super-hyperfine lines due to the nitrogen nuclei, from which A_N values were evaluated, appear on the $g_{\perp}$ positions. The solution spectra (A) also shows four hyperfine lines due to the copper atom and additional splittings caused by the nitrogen nuclei in the upper field. The $g_{\perp}$ and $A_{\perp}$ values for the frozen sample were evaluated by the simulation method of hyperfine structure appeared in the upper field. The spin Hamiltonian parameters obtained in this work are almost comparable with the data for the phthalocyanine and porphyrin complexes taken from the literature, as shown in Table 2.

One of the σ-molecular orbitals for coordination in D_{4h} symmetry can be represested as follows:

$$\Psi_{\mathrm{B}_{1g}} = \alpha d_{x^2-y^2} - 1/2\,\alpha'\,[-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}]$$

The sigma-bonding parameter α^2 can be calculated by the following equation given by Kivelson and Neiman:14)

$$\alpha^2 = -(A_{\parallel}/P) + (g_{\parallel} - 2) + 3/7\,(g_{\perp} - 2) + 0.04$$

where 0.036 was given to P. Judging from α^2 values, the coordinate bond character seems to be comparable to those in the phthalocyanine and porphyrin complexes.

X-Ray Powder Diffraction Patterns. The X-ray powder diffraction patterns for the copper, zinc, nickel, and cobalt complexes of BLD are shown in Fig. 9. The general feature of the diffraction pattern for the copper complex has a close resemblance to that for the nickel complex although the careful comparison reveals some minor difference in their relative intensity. On the other hand, the powder pattern for the zinc complex is found to be almost identical with that for the corresponding cobalt complex. As a result, stacking manner of the copper complex in crystalline state is close to or almost identical to that of the nickel complex; so is the zinc complex to the cobalt complex.

These results provide another evidence for the structural properties of the present complexes: the copper complex involves the coordinate bonds of square-planar orientation in a monomeric form, while the zinc complex consists of tetrahedrally coordinated bonds in a binuclear form.

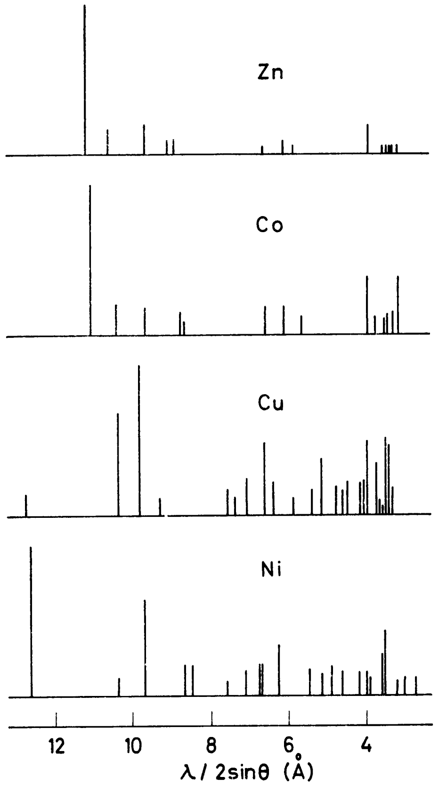

Fig. 9. X-Ray powder diffraction patterns of the BLD complexes of bivalent metals. The relative diffraction intensity at a Bragg angle θ is represented by the height of vertical lines.

Structure of the Metal Complexes. The elemental analysis of the copper complex is consistent with a ligand to metal ratio of 1 : 1 with no additional ions or species. The molecular weight determination by means of vapor pressure osmometer indicates this complex is monomeric. The infrared bands characteristic of asymmetric stretching vibration of the carbethoxy groups at positions 8 and 12 are different in their positions from those observed for the BLD free base and the corresponding zinc and cobalt com-

TABLE 2. SPIN HAMILTONIAN PARAMETERS FOR THE COPPER COMPLEXES

Ligand[a]	Diluent	Temp.[b]	g_0	$g_{\parallel}$	$g_{\perp}$	$A_0\times10^4$, cm^{-1}	$A_{\parallel}\times10^4$, cm^{-1}	$A_{\perp}\times10^4$, cm^{-1}	$A_N\times10^4$, cm^{-1}	α^2	Ref.
BLD	xylene-benzene[c] (6 : 4)	R	2.102			76.2			13.5		This work
BLD	xylene-benzene[c] (6 : 4)	77°K		2.197	2.042		177	48.1	14.2	0.75	This work
BLD	Ni-BLD	R		2.212			180		13.5		This work
PHC	H_2SO_4	G		2.174	2.045		202			0.78	14
PHC	H_2SO_4	136°K		2.180	2.037					0.72	16
EPP	Caster oil, benzene		2.097	2.169	2.061		188	39		0.74	15

a) BLD, the present biladiene-ac; PHC, phthalocyanine; EPP, ethioporphyrin II.
b) R, room temperature; G, frozen to glass state.
c) Concentration of the complex; $\sim10^{-4}$ mol/l at room temperature.

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14) D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 150 (1961).

15) E. M. Roberts and W. S. Koski, *J. Amer. Chem. Soc.*, **82**, 3006 (1960).

16) E. M. Roberts and W. S. Koski, *ibid.*, **83**, 1865 (1961).

plexes, but in conformity with those for the nickel complex of square-planar coordination. The appearance of the ligand-field bands at 701 and 752 mμ also indicates that the copper atom is placed approximately in a square-planar ligand-field. The overall feature of the ESR spectrum and spin Hamiltonian parameters obtained therefrom ($g_{\parallel}$, $g_{\perp}$ and A values) are consistent with the square-planar coordination. Since the X-ray diffraction pattern of the powdered sample is closely related to that of the nickel complex, this data may give another support to the structure. In conclusion, these experimental facts as a whole are consistent with the square-planar coordination of the copper atom with the pyrrolic nitrogens of BLD in a monomeric manner (IV).

By referring to the elemental analysis and the molecular weight measurement of the zinc complex, the complex is binuclear with a ligand to metal ratio of 2 : 2. The infrared bands due to asymmetric stretching vibration of the ester groups provide an evidence that the carbethoxy groups at positions 8 and 12 are free from steric strain to an extent expected in the BLD free base and in the corresponding cobalt complex of tetrahedral coordination as explained in the previous section. The dimeric nature of the complex was also demonstrated by NMR spectroscopy. All the upfield shifts of proton signals through coordination can be predicted on the basis of binuclear complex formation. Although a dimeric form with tetrahedral coordination shown by structure III was put forward previously for the cobalt complex,[2)] this turns out to be unsatisfactory for explaining the experimental data reported in this work and deserves an appropriate revision as depicted in Fig. 5. The X-ray powder diffraction pattern was indentical with that of the cobalt complex which assumes tetrahedral configuration around the central metal atom with dimeric structure. As a result, the most plausible structure for the zinc complex is the binuclear form with tetrahedral coordination of the metal atom, identical with the corresponding cobalt complex, as depicted in Fig. 5.