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Preparation and Properties of Di-μ-alkoxo-bis(3-alkyl-5-methylsalicylaldehydato)dicopper(II)

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In this paper, the syntheses of copper(II) complexes of 3-alkylsalicylaldehydes, B, as well as the syntheses and properties of dimeric copper(II) complexes, C, with bridged alkoxy groups are reported.

In the course of our studies of the effects of large-membered chelate rings on the stabilities of such complexes as A, copper(II) complexes of 3-alkylsalicylaldehydes were synthesized as reference compounds. The copper(II) complexes thus obtained were normal, monomeric copper(II) chelates, B (ligand: Cu=2 : 1); when these copper(II) complexes, B, were refluxed with alcohol without any bases, the monomeric complexes could be converted to dimeric copper(II) complexes, C. The structures of the dimeric copper(II) complexes, C, with bridged alkoxy groups were verified by the study of the infrared spectrum, the ultraviolet spectrum, the nuclear magnetic resonance spectrum, by elementary analysis, a molecular-weight determination, electrophoresis, and by considering the magnetic moment of di-μ-ethoxo-bis(3-ethyl-5-methylsalicylaldehydato)dicopper(II), XVII, as a representative of the dimeric copper(II) complexes, C.

Several complexes containing alkoxide, especially methoxide, have been reported,[1,2] but very few

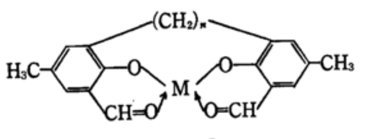
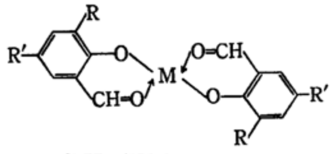


Fig. 1. [A]



$R'=H$; $R=t\text{-}C_4H_9$ (XII).
$R'=CH_3$; $R=CH_3$ (VIII), $R=C_2H_5$ (IX), $R=n\text{-}C_3H_7$ (X), $R=n\text{-}C_4H_9$ (XI), $R=n\text{-}C_5H_{11}$ (XIII), $R=cyclo\text{-}C_6H_{11}$ (IV).

Fig. 2. [B]

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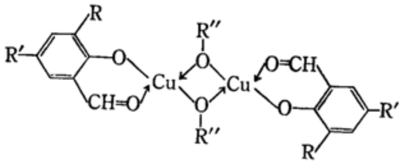
[1] J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, **4**, 1657 (1965).

[2] R. M. Klein and J. C. Bailar, Jr., *ibid.*, **2**, 1187 (1963).

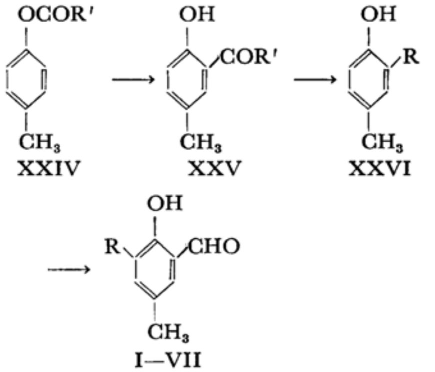


$R''=C_2H_5$, $R'=H$; $R=t\text{-}C_4H_9$ (XXI)
$R''=C_2H_5$, $R'=CH_3$; $R=CH_3$ (XV),
$R=C_2H_5$ (XVII), $R=n\text{-}C_3H_7$ (XIX),
$R=n\text{-}C_4H_9$ (XX), $R=n\text{-}C_5H_{11}$ (XXII),
$R=cyclo\text{-}C_6H_{11}$ (XXIII)
$R''=CH_3$, $R'=CH_3$; $R=C_2H_5$ (XVI)
$R''=n\text{-}C_8H_{17}$, $R'=CH_3$; $R=C_2H_5$ (XVIII)

Fig. 3. [C]

stable dimeric copper(II) complexes with bridged alkoxy groups have been reported. In some cases,[1] dimeric copper(II) complexes have been obtained by refluxing with a base such as potassium hydroxide. In these experiments, the dimeric copper(II) complexes could be obtained by merely refluxing with alcohol without any bases. In the case of monomeric copper(II) complexes of salicylaldehydes without an alkyl group at the 3 position, such as salicylaldehyde or 5-methylsalicylaldehyde, dimeric copper(II) complexes could not be isolated by refluxing in alcohol without any bases.[3] Therefore, the alkyl group in the 3 position must have exerted some steric effects.

Four 3-alkyl-5-methylsalicylaldehydes, II, III, IV, and VI, were synthesized as is shown in Fig. 4 by the Duff reaction of 2-alkyl-4-methylphenols, XXVI,[4] with boric acid and hexamethylenetetramine in glycerol. The 2-alkyl-4-methylphenols were synthesized by the Clemmensen reduction of 2-acyl-4-methylphenols, XXV, which had themselves been obtained from the aryl ester, XXIV, by the Fries rearrangement.



XXIV $R'=CH_3$, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$
XXV $R'=CH_3$, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$
XXVI $R=C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$

Fig. 4. Synthetic route of aldehydes I—VII.

TABLE 1. C–O STRETCHING VIBRATION OF THE BRIDGED ALKOXY GROUPS OVER THE 1040—1070 cm^{-1} RANGE

	R	R″	C–O, cm^{-1}
XV	CH_3	C_2H_5	1060, 1048
XVII	C_2H_5	C_2H_5	1068, 1054
XIX	$n\text{-}C_3H_7$	C_2H_5	1059, 1050
XX	$n\text{-}C_4H_9$	C_2H_5	1060, 1054
XXI*	$t\text{-}C_4H_9$	C_2H_5	1055
XXII	$n\text{-}C_5H_{11}$	C_2H_5	1063, 1055
XXIII	$cyclo\text{-}C_6H_{11}$	C_2H_5	1060, 1050
XVI	C_2H_5	CH_3	1070, 1040
XVIII	C_2H_5	$n\text{-}C_8H_{17}$	1069, 1055

* No methyl group in the 5 position.

In each case, a monomeric copper(II) complex, B, was obtained by the addition of an ethanolic solution of a ligand. By refluxing the brown-colored monomeric complexs, B, with alcohol, green complexes were obtained. The green crystals thus obtained were suggested to be dimeric

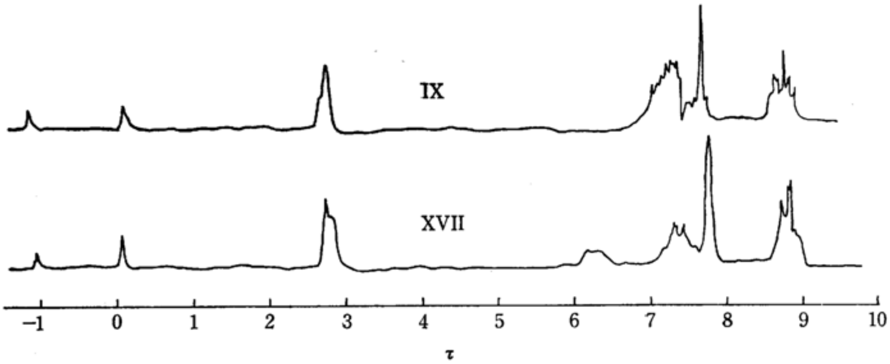


Fig. 5. The NMR spectra of the monomeric complex, IX and the dimeric complex, XVII.

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[3] The dimeric complexes can be obtained by refluxing in alcohol with potassium hydroxide; T. Shono, M. Mori and K. Shinra, Paper presented at the 18th Symposium on Coordination Chemistry, Kyoto, October, 1968.

[4] The $R=CH_3$ in XXVI was commercially obtained. The $R=cyclo\text{-}C_6H_{11}$ in XXVI was obtained by the Friedel-Crafts reaction of *p*-cresol with cyclohexene. See Y. Koike, H. Okawa, T. Inazu and T. Yoshino, *Mem. Fac. Sci., Kyushu Univ., Ser. C, Chem.*, **6**, 5 (1967).

by elementary analyses and by molecular-weight determinations. In the infrared spectra of the dimeric complexes, C, the bands over the 1040—1070 cm^{-1} range are assigned to the C–O stretching vibration of the bridged alkoxy groups, which are not observed in the case of the monomeric complexes, B. The data of the infrared spectra are given in Table 1.

The magnetic moments of the compounds were calculated using the expression; $\mu_{eff}=(8\chi_A T)^{1/2}$. The value obtained, 1.36 B. M., for the dimeric copper(II) complex, XVII, was considerably below the value for one unpaired electron. The value obtained for the monomeric copper(II) complex, IX, was 2.03 B. M. The dimeric nature, the low magnetic moment, and the tendency of copper(II) to achieve four-coordination suggest that there are bridging groups present in the complex.

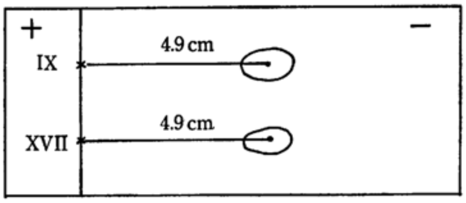

Fig. 6. Paper electrophoresis of the monomeric complex, IX and the dimeric complex, XVII.

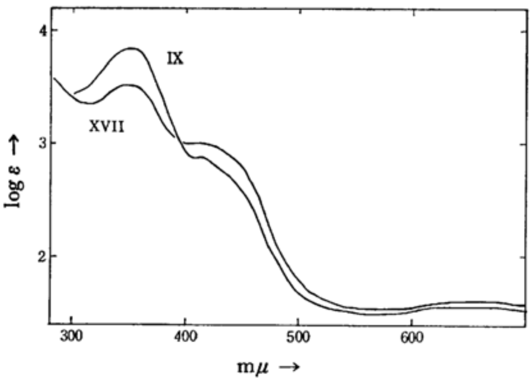

Fig. 7. Visible and ultraviolet spectra of the monomeric complex, IX, and the dimeric complex, XVII, in benzene.

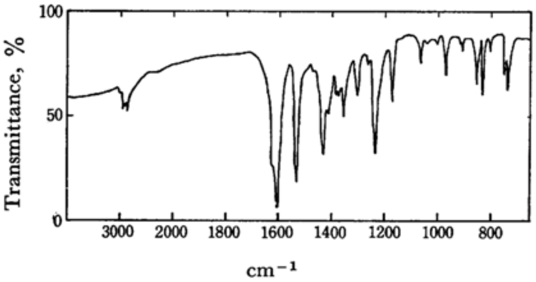

Fig. 8. Infrared spectrum of the monomeric complex, IX, in KBr disk.

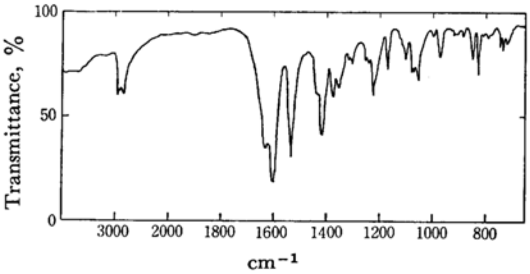

Fig. 9. Infrared spectrum of the dimeric complex, XVII, in KBr disk.

The NMR spectrum of the dimeric copper(II) complex, XVII, was in accord with that assumed for the dimeric structure; $\tau=8.75$ multiplet for terminal methyl protons at the 3 position and the bridged ethoxy groups, $\tau=7.67$ singlet for methyl at the 5 position, $\tau=7.40$ quartet for methylene protons at the 3 position, $\tau=6.27$ broad for methylene groups of the bridged ethoxy groups, and $\tau=0.12$ singlet for aldehyde protons. In the NMR spectrum of the monomeric copper(II) complex, IX, the absorption bands in the region $\tau=6.3$ were not observed, while other bands were observed at comparative positions. In both cases, protons for the dissociated salicylaldehyde, $\tau=-1.13$ for the dimeric complex, XVII, and -1.17

TABLE 2. PROPERTIES OF ALDEHYDES

	Aldehyde		Cryst. form*	Mp, Bp	Yield %
	R	R′			
I	CH_3	CH_3	py. liq	99—111°C/22 mmHg	19.6
II	C_2H_5	CH_3	py. liq	133—137°C/33 mmHg	23
III	n-C_3H_7	CH_3	py. liq	140—148°C/34 mmHg	21
IV	n-C_4H_9	CH_3	py. liq	141—153°C/38 mmHg	10.4
V	t-C_4H_9	H	py. liq	126—131°C/22 mmHg	4
VI	n-C_5H_{11}	CH_3	py. liq	163—184°C/40 mmHg	13.6
VII	*cyclo*-C_6H_{11}	CH_3	py. n.	127°C	41

* b=brown, g=green, liq=liquid, n=needles, p=powder, pl=plates, py=pale yellow y=yellowish.

TABLE 3. PROPERTIES AND ANALYTICAL DATA OF THE MONOMERIC COMPLEXES, B

	Cryst. form*	Mp	Formula	Analyses, %						Yield %
				Found			Calcd			
				C	H	Cu	C	H	Cu	
VIII	b.n.	231—232°C	$C_{18}H_{18}O_4Cu$	59.89	5.18	17.43	59.74	5.01	17.56	54.2
IX	b.n.	152—154°C	$C_{20}H_{22}O_4Cu$	61.50	5.89	16.33	61.60	5.69	16.30	27
X	b.n.	173—174°C (decomp)	$C_{22}H_{26}O_4Cu$	62.97	6.27	15.10	63.22	6.27	15.20	29.8
XI	b.n.	149—151°C (decomp)	$C_{24}H_{30}O_4Cu$	64.53	6.74	14.26	64.63	6.78	14.25	29
XII	b.pl.	226.5—228°C	$C_{22}H_{26}O_4Cu$	63.00	6.27	14.96	63.22	6.27	15.20	29.2
XIII	b.n.	142—145.5°C (decomp)	$C_{26}H_{34}O_4Cu$	65.75	7.46	13.33	65.87	7.23	13.40	19.7
XIV	b.n.	232—233°C	$C_{28}H_{34}O_4Cu$	67.51	6.92	12.52	67.52	6.88	12.76	62.6

* b=brown, g=green, liq=liquid, n=needles, p=powder, pl=plates, py=pale yellow, y=yellowish.

TABLE 4. PROPERTIES AND ANALYTICAL DATA OF THE DIMERIC COMPLEXES, C

	Cryst. form*	Mp	Formula	Analyses, %						Mol wt		Yield %
				Found			Calcd			Found	Calcd	
				C	H	Cu	C	H	Cu			
XV	g.p.	182—196°C (decomp)	$C_{22}H_{28}O_6Cu_2$	50.95	5.75	24.89	51.20	5.47	24.65		515.56	48.1
XVI	y.g.p.	202°C (decomp)	$C_{22}H_{28}O_6Cu_2$	51.04	5.45		51.26	5.47	24.65		515.56	
XVII	g.n.	180—183°C	$C_{24}H_{32}O_6Cu_2$	52.78	5.99	23.64	53.03	5.93	23.38	520.1	543.61	73.9
XVIII	g.p.	108°C (decomp)	$C_{36}H_{56}O_6Cu_2$	59.40	7.93	18.80	60.74	7.93	17.85		711.89	
XIX	g.p.	171—172°C	$C_{26}H_{36}O_6Cu_2$	54.72	6.57	22.38	54.63	6.34	22.23	589	571.67	75.5
XX	y.g.n.	165°C	$C_{28}H_{40}O_6Cu_2$	55.82	6.81	21.00	56.08	6.72	21.19		599.72	
XXI	y.g.n.	171—181.5°C	$C_{26}H_{36}O_6Cu_2$	54.51	6.64	20.64	54.63	6.35	22.23		571.67	56.4
XXII	g.p.	132—133°C	$C_{30}H_{44}O_6Cu_2$	57.22	7.36	20.18	57.40	7.06	20.24		627.77	54.9
XXIII	y.g.p.	216°C (decomp)	$C_{32}H_{44}O_6Cu_2$	58.61	7.19	19.67	58.97	6.80	19.50	696	651.80	59.9

* b=brown, g=green, liq=liquid, n=needles, p=powder, pl=plates, py=pale yellow, y=yellowish.

for the monomeric complex, IX, were observed.

A large number of copper(II) compounds, including bissalicylaldehydato copper(II), are square-planar. The visible spectra of the IX and XVII complexes consist of a broad band centered around 650 mμ. The absorption is similar in wavelength and in intensity to that of square-planar complexes of copper(II).[1] The close resemblance of the ultraviolet and visible spectrum of the dimeric copper(II) complex, XVII, to that of the monomeric copper(II) complex, IX, revealed that the dimeric complex, XVII, is square-planar. With the aid of paper electrophoresis, it was proved that copper atoms in the dimeric complex, XVII, are not in a reduced univalent state. All the experimental evidence is consistent with a planar, dimeric structure.

Experimental

All the melting points are uncorrected. The physical properties and analytical data of the products are summarized in Tables 2, 3, and 4. The ultraviolet and visible spectra were measured on a Hitachi EPS-3T spectrophotometer. The infrared spectra were measured on a Hitachi EPI-S2 spectrophotometer. The NMR spectra were recorded on a Varian Associates A-60 model, using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. The molecular weights were obtained with a Hitachi 115 vapor-pressure osmometer, using benzene as the solvent.

Magnetic Moment Determination. The magnetic susceptibilities of the compounds were measured with a Gouy balance at 27°C. The corrected molar susceptibilities were 771.5×10^{-6} c.g.s. unit for the dimeric complex, XVII, and 1725.4×10^{-6} c.g.s. unit for the monomeric complex, IX.

Paper Electrophoresis. Toyo Roshi No. 51 filter paper was used, with a solvent system of 8% formic acid - acetic acid - methanol - water (1 : 3 : 6 : 10 by vol) (600 V, 3 mA, 30 min). Without further treatment, pale blue spots of cupric ions were obtained.

3-Ethyl-5-methylsalicylaldehyde, II. The mixture of 150 g of glycerol and 35 g of boric acid was heated on a water bath under diminshed pressure for 2 hr and then on an oil bath at 200°C for 30 min. To the mixture there were added 25 g of hexamethylenetetramine and 36.2 g of 2-ethyl-*p*-cresol. The mixture thus obtained was heated at 150—165°C for 50 min. After cooling, 25 m*l* of concentrated sulfuric acid in 75 m*l* of water was added to the reaction mixture. The mixture was steam-distilled, and the 3-ethyl-5-methylsalicylaldehyde thus obtained was extracted with ether. The organic layer was washed with water and dried over anhydrous sodium sulfate, and the ether was removed. The residual oil was distilled, bp 122—124°C/20 mmHg, in a 12.5% yield (5.45 g).

Bis(3-ethyl-5-methylsalicylaldehydato)copper(II), IX. A solution of 2.00 g of 3-ethyl-5-methylsalicylaldehyde in 10 m*l* of ethanol was mixed with a solution of 1.60 g of copper(II) acetate monohydrate in 30 m*l* of ethanol. The mixed solution was left standing under diminished pressure at room temperature. The brown needles thus formed were collected and washed with a little ethanol. Yield, 516 mg, 21.7%. Mp 152—154°C.

Conversion of the Monomeric Complex, IX, to the Dimeric Complex, XVII. A mixture of 305 mg of the monomeric complex, IX, and 30 m*l* of ethanol was refluxed for 30 min. After cooling, 157 mg of green needles of the dimeric complex, XVII, were collected and washed with a little ethanol. They were soluble in chloroform and insoluble in water.