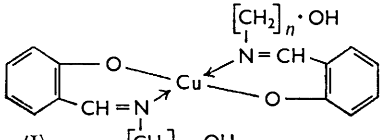
777. *Reactions of Co-ordinated Ligands. Part II.*[1] *Reactions of Co-ordinated Alcohols, Esters, and Ethers*

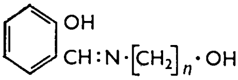
By R. P. Houghton and D. J. Pointer

Some reactions of copper chelates obtained by condensation of bis(salicylaldehydato)copper(II) with amino-alcohols, esters of amino-alcohols, and amino-ethers are described. It is suggested that the reactions that occur in neutral solution involve ionic species in which a copper ion is co-ordinated to a hydroxyl, ester, or ether group.

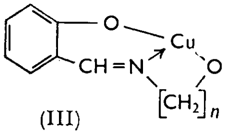
In Part I [1] we showed that the copper chelates prepared by condensation of bis(salicylaldehydato)copper(II) with α- and β-amino-esters readily undergo ester-exchange reactions and hydrolysis under neutral conditions, and that these reactions are accelerated by the introduction of substituents into the amino-ester moities. It was suggested that the reactions involved ionisation of the chelates followed by co-ordination of an ester group with a copper ion, and that the faster rates of reaction of the substituted chelates were due to the rates of ionisation being increased by steric hindrance. In this Paper, we describe some reactions of chelates obtained by condensation of bis(salicylaldehydato)copper(II) with amino-alcohols and esters of amino-alcohols. These reactions, which are similarly explained by ionic mechanisms, also proceed at a faster rate if the chelates are substituted in certain positions. Some reactions of copper chelates derived from amino-ethers are also described.



(I)



(II)



(III)

Condensation of the appropriate ω-amino-alcohols with bis(salicylaldehydato)copper(II) in benzene or ethanol gave the chelates (I; $n = 2$, 3, and 4) which when refluxed with ethylenediaminetetra-acetic acid in methanol gave the parent ligands (II; $n = 2$, 3, and 4, respectively). Treatment of the chelate (I; $n = 3$) with aqueous sodium hydroxide or sodium ethoxide in ethanol gave the chelate (III, $n = 3$; 1 mol.) and the ligand (II, $n = 3$; 1 mol.), but in the presence of cupric acetate only the salt (III, $n = 3$; 2 mol.) was formed. Similarly, a mixture of the chelate (I; $n = 2$), cupric acetate, and sodium hydroxide in ethanol afforded the chelate (III; $n = 2$), but the higher homologue (I; $n = 4$) was unaffected by treatment with base. The chelates (III; $n = 2$ and 3) are formulated as shown because, although they do not contain hydroxyl groups (infrared spectra), they give the ligands (II; $n = 2$ and 3, respectively) when treated with ethylenediaminetetra-acetic acid. In these chelates, the fourth co-ordination position of the copper atoms

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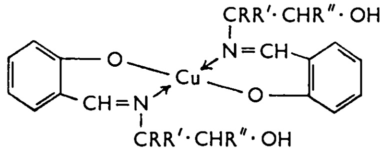
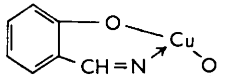
[1] Part I, R. P. Houghton and D. J. Pointer, *J.*, **1964**, **3302**.

is probably filled by the compounds existing in the form of dimers as found by Barclay, Harris, Hoskins, and Kokot[2] for the chelate (XV) and related compounds. Their formation by the action of a base on the chelates (I; $n = 2$ and 3) probably occurs by removal of a proton from one of the hydroxyl groups followed by attack of the metal atom by the resultant alkoxide ion and displacement of one of the ligands as an anion.

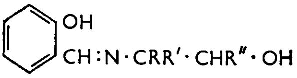
When the chelate (I; $n = 3$) was refluxed in ethanol or other organic solvents, a mixture of the starting material, the chelate (III; $n = 3$), and the phenol (II; $n = 3$) was formed. The same mixture was also formed when the last two compounds were refluxed together in ethanol, which indicated that the reaction was reversible. The chelates (I; $n = 2$ and 4) were unchanged when treated with hot solvents, but in contrast the substituted systems (IV*b* and *c*) were so unstable in solution that attempts to prepare them by the usual condensation method gave only the chelates (V*b* and *c*) and the corresponding phenols (VI*b* and *c*). Treatment of bis(salicylaldato)copper(II) (1 mol.) in benzene with 2-amino-1-phenylpropan-1-ol (1 mol.) gave salicylaldehyde and the chelate (V*d*), which with ethylenediaminetetra-acetic acid gave the phenol (VI*d*). The chelate (IV*a*) was comparatively stable, for it was prepared without difficulty, and formed the chelate (V*a*) to only a small extent when refluxed in organic solvents.



(IV)

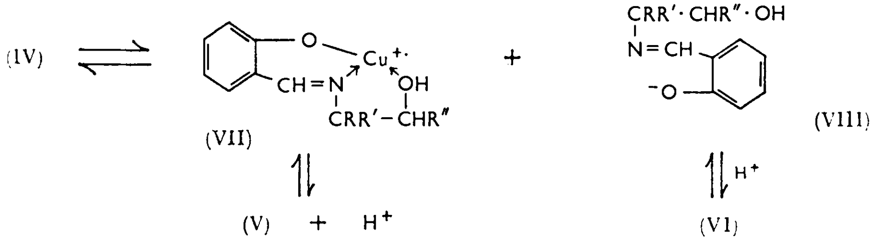


(V)



(VI)

	a	*b*	*c*	*d*
R	H	H	Me	H
R′	H	Me	Me	Me
R″	Me	H	H	Ph



Scheme (A)

Although the transformations described above may involve traces of alkali present in the solvents, and may proceed by the mechanism suggested earlier, it is more likely that they proceed by ionisation of the chelates (IV), followed by interaction in the cation [VII; see Scheme (A)] between the copper ion and the hydroxyl group, and subsequent loss of a proton to the anion (VIII). The instability of the substituted chelates (IV*b* and *c*) almost certainly arises from steric hindrance between the phenolic oxygen atoms and the CRR′·CHR″·OH groups. Molecular models indicate that the steric hindrance is relieved when these compounds are converted into the corresponding chelates of type (V), hence the equilibrium (IV $\rightleftharpoons$ V + VI) would be expected to lie further to the right-hand side with the substituted chelates than with the parent chelate (I; $n = 2$). The fact that the chelate (IV*a*) is considerably more stable than the isomer (IV*b*) suggests that the former compound is less sterically hindered than the latter, and this is also indicated by molecular models.

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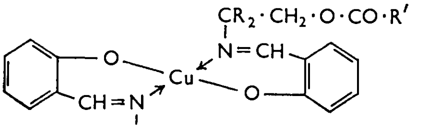
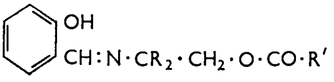
[2] G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc.*, 1961, 264.

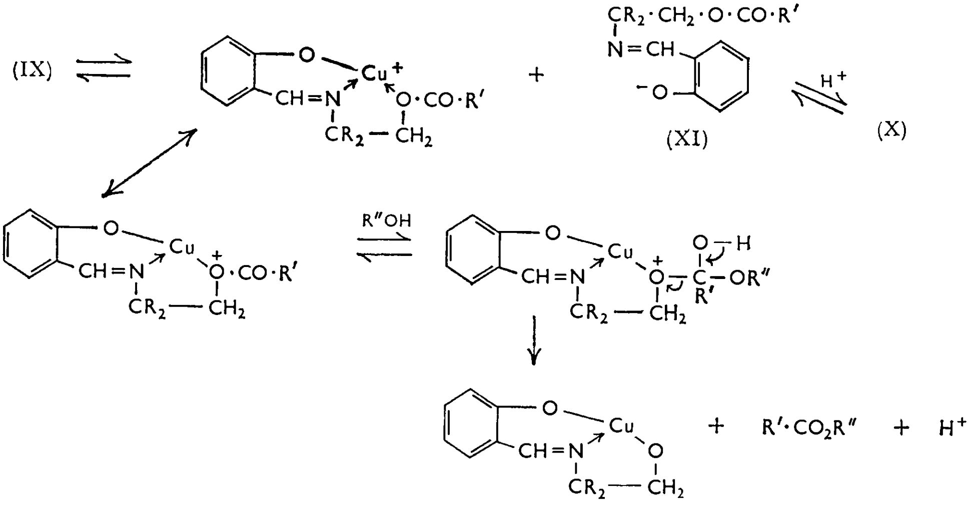
The chelate (IX*a*) was prepared by warming a mixture of bis(salicyaldehydato)-copper(II), sodium acetate, and 2-acetoxyethylamine hydrochloride in ethanol. This method was used because attempts to prepare 2-acetoxyethylamine from its hydrochloride gave only the rearranged product, *N*-acetylethanolamine, cf. Porter, Rydon, and Schofield.[3] When the chelate was refluxed in 20% aqueous dioxan (v/v) for 24 hr. the


(IX)

a: R = H, R′ = Me
b: R = Me, R′ = Ph


(X)

chelate (III; $n = 2$) was obtained (93%) together with *N*-acetylethanolamine. Under the same conditions, the chelate (I; $n = 2$) was recovered unchanged, which indicated that this chelate was not an intermediate in the reaction. As this type of reaction was expected to be facilitated by the introduction of substituents into the amino-ester moities the chelate (IX*b*) was prepared by the usual condensation method. This chelate is maroon in colour, which indicates that it has a pseudo-tetrahedral structure,[4] presumably because steric hindrance prevents the ligands from assuming the usual square planar arrangement around the metal atom. When refluxed in 20% aqueous dioxan (v/v) for 1½ hr. the chelate was hydrolysed to give benzoic acid, the chelate (V*c*), and the phenol (X*b*). The last two compounds were also obtained, together with ethyl benzoate, when an ester-exchange reaction was carried out with the chelate in refluxing ethanol. The rapidity of the last reaction, which was complete within 2 min., was remarkable.



Scheme (B)

The products formed in the above hydrolyses and ester-exchange reaction are accounted for by the mechanism shown in Scheme B. The *N*-acetylethanolamine obtained from the chelate (IX*a*) was presumably formed by hydrolysis of the phenol (X*a*), an expected product of the reaction, followed by rearrangement of the resultant 2-acetoxyethylamine. It is noteworthy that the experiments constitute evidence that a metal ion may co-ordinate with

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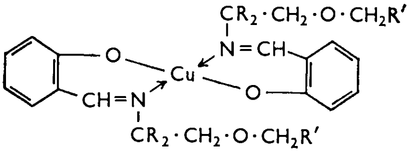
[3] G. R. Porter, H. N. Rydon, and J. A. Schofield, *J.*, 1960, 2686.

[4] L. Sacconi and M. Ciampolini, *J.*, 1964, 276.

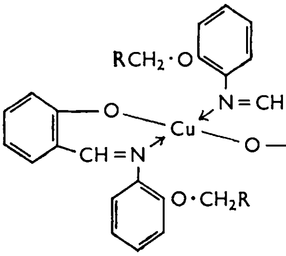
an ester group through the alkoxy-oxygen atom, as well as through the carbonyl oxygen atom as is usually observed, cf. Lappert.[5]



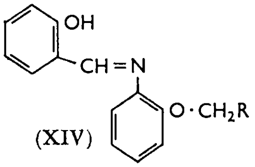
(XII)

a: R = H, R′ = H
b: R = H, R′ = Ph
c: R = Me, R′ = Ph

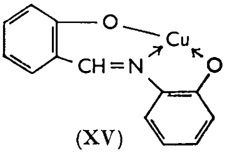
As metal salts are known to form complexes with ethers,[6] it seemed possible that chelates of type (XII) might undergo reactions involving ionic species in which an ether group was co-ordinated to a copper ion. The chelates (XII; *a*—*c*) were prepared by the usual method, but in refluxing solvents the first two compounds were unchanged, and the last, which was a maroon-coloured solid, was decomposed to give fragments, which were not identified. Some success, however, was obtained with the chelates (XIII; R = H and Ph), which were prepared as buff-coloured solids by treatment of the Schiff bases (XIV; R = H and Ph, respectively) with cupric acetate. When refluxed for 24 hr., in dimethylformamide or chlorobenzene, or heated (200°) in dimethyl sulphoxide, the chelate (XIII; R = H) was partly converted (28, 8, and 24%, respectively) into the chelate (XV), an authentic sample of which was prepared by the method of Pfeiffer *et al.*[7] When the chelate (XIII; R = Ph) was refluxed for 24 hr. in dimethylformamide the chelate (XV) was obtained in 64% yield, together with the phenol (XIV; R = Ph; 87%). In one experiment benzyl alcohol was also isolated, although in very low yield, as the α-naphthylurethane. These products may be rationalised in terms of a mechanism similar to that shown in Scheme A.



(XIII)



(XIV)



(XV)

Experimental

Infrared spectra of chelates and ligands were measured on Nujol mulls and chloroform solutions, respectively. 4-Aminobutan-1-ol,[8] 2-benzyloxyethylamine,[9] and 1,1-dimethyl-2-benzyloxyethylamine [10] were prepared by the methods described in the literature.

Bis-[N-(*3-hydroxypropyl*)*salicylideneaminato*]*copper*(II) (I; *n* = 3).—3-Aminopropan-1-ol (5·0 g.) was added with stirring to a mixture of bis(salicylaldehydato)copper(II) (10·0 g.) and benzene (100 ml.). The mixture was warmed (~50°) for 2—3 min., and then cooled and filtered to give the *chelate* (13·5 g., 98%) as olive-green needles, m. p. 115° (from benzene) (Found: C, 57·0; H, 5·6; Cu, 15·2; N, 6·6. $C_{20}H_{24}CuN_2O_4$ requires C, 57·2; H, 5·8; Cu, 15·1; N, 6·7%). The *chelates* listed in Table 1 were prepared similarly.

N-(*3-Hydroxypropyl*)*salicylideneamine* (II; *n* = 3).—The preceding chelate (2·17 g.) and ethylenediaminetetra-acetic acid (1·42 g.) were refluxed in methanol (30 ml.) for 30 min. The mixture was cooled and filtered, and the solvent was removed from the filtrate under reduced pressure. The residue was triturated with light petroleum (b. p. 60—80°) to give the *phenol*

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[5] M. F. Lappert, *J.*, 1961, 817.
[6] R. L. Burwell, *Chem. Rev.*, 1954, **54**, 615.
[7] P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. prakt. Chem.*, 1937, **149**, 217.
[8] E. D. Bergmann and A. Kaluszyner, *Rec. Trav. chim.*, 1959, **78**, 331.
[9] L. C. Lappas and G. L. Jenkins, *J. Amer. Pharmaceut. Assoc.* (*Sci. Edn.*), 1952, **41**, 257.
[10] V. Burckhardt, W. Kundig, and P. Siebrer, *Helv. Chim. Acta*, 1952, **35**, 1437.

Table 1

Chelates

Chelate	Yield (%)	M. p.	Found (%)				Formula	Required (%)			
			C	H	Cu	N		C	H	Cu	N
(I; *n* = 2)	90 (a)	172—173° (c)	55·3	5·3	15·8	7·05	$C_{15}H_{20}CuN_2O_4$	55·2	5·1	16·2	7·15
(I; *n* = 4)	66 (b)	101—103 (d)	58·75	6·2	13·9	6·3	$C_{22}H_{28}CuN_2O_4$	59·0	6·3	14·2	6·3
(IV*a*)	99 (a)	209—210 (c)	57·2	5·8	15·3	6·6	$C_{20}H_{24}CuN_2O_4$	57·2	5·8	15·1	6·7
(XII*a*)	93 (b)	121—122 (e)	57·4	6·0	15·0	6·4	$C_{20}H_{24}CuN_2O_4$	57·2	5·8	15·1	6·7
(XII*b*)	96 (b)	115 (c)	67·4	5·7	11·05	4·5	$C_{32}H_{32}CuN_2O_4$	67·2.	5·6	11·1	4·9
(XII*c*)	80 (b)	69—70 (f)	68·8	6·5	10·1	4·6	$C_{36}H_{40}CuN_2O_4$	68·8	6·4	10·1	4·5

(a) Prepd. in benzene. (b) Prepd. in ethanol. (c) From benzene. (d) From ethanol. (e) From diethyl ether. (f) From light petroleum (b. p. 60—80°).

(1·37 g., 74%) as a yellow solid, m. p. 43° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 67·0; H, 7·2; N, 7·8. $C_{10}H_{13}NO_2$ requires C, 67·0; H, 7·3; N, 7·8%).

Table 2 shows the *phenols* prepared in a similar manner.

Table 2

Phenols

Phenol	Yield (%)	B. p./mm. or m. p.	n_D	Found (%)			Formula	Required (%)		
				C	H	N		C	H	N
(II; *n* = 2)	72	124—126°/0·5	1·6062 (22°)	65·3	6·7	8·3	$C_9H_{11}NO_2$	65·4	6·7	8·5
(II; *n* = 4)	53	134—136/0·4	1·5742 (20°)	67·4	7·7	7·1	$C_{11}H_{15}NO_2$	68·4	7·8	7·3
(VI*a*)	58	M. p. 65—67°		67·2	7·3	7·9	$C_{10}H_{13}NO_2$	67·0	7·3	7·8

Preparation and Reactions of N-(3-*Hydroxypropylato*)*salicylideneaminatocopper*(II) (III; *n* = 3).—(*a*) The chelate (I; *n* = 3) (1·52 g.) was refluxed in ethanol (30 ml.) for 30 min., and the mixture was cooled and filtered to give the *chelate* (0·53 g., 82% based on recovered starting material), which crystallised from dioxan as a deep purple-coloured solid, m. p. 282° (Found: C, 50·1; H, 4·7; Cu, 26·1; N, 5·8. $C_{10}H_{11}CuNO_2$ requires C, 49·9; H, 4·6; Cu, 26·4; N, 5·8%). The solvent was removed from the filtrate under reduced pressure and the residue was extracted with hot light petroleum (b. p. 60—80°) to leave unchanged starting material (0·40 g., 26%). The light petroleum extract was cooled to give the phenol (II; *n* = 3) (0·31 g., 65% based on recovered starting material), m. p. 43°. The last two products were identified by their infrared (i.r.) spectra.

(*b*) A mixture of the chelate (I; *n* = 3) (1·53 g.) and sodium ethoxide (from sodium, 2·00 g.) in ethanol (40 ml.) was shaken for 5 min. and then filtered to give the chelate (782 mg., 91%). The filtrate was neutralised (litmus) with 5N-hydrochloric acid and concentrated under reduced pressure to a volume of about 10 ml. The solid (NaCl) was removed by filtration and the filtrate was extracted with chloroform (3 × 10 ml.) to give the phenol (II; *n* = 3) (538 mg., 84%). The i.r. spectra of both products were identical with those of authentic samples.

(*c*) Sodium ethoxide (from sodium, 1·00 g.) in ethanol (20 ml.) was added to a suspension of the chelate (I; *n* = 3) (4·20 g.) and cupric acetate (2·54 g.) in ethanol (50 ml.). The mixture was shaken for several min. and then filtered to give the chelate (4·45 g., 92%).

(*d*) The chelate (240 mg.) and the phenol (II; *n* = 3) (180 mg.) were refluxed in ethanol (30 ml.) for 12 hr. The mixture was cooled and filtered to give unchanged chelate (143 mg.), and the solvent was removed from the filtrate under reduced pressure. The residue was extracted with hot light petroleum (b. p. 60—80°) to remove unchanged phenol, then crystallised from benzene to give the chelate (I; *n* = 3) (125 mg., 74% based on recovered chelate) which was identified by its i.r. spectrum.

(*e*) The chelate (1·91 g.) and ethylenediaminetetra-acetic acid (2·3 g.) were refluxed in methanol (30 ml.) for 1½ hr. The mixture was cooled and filtered and the solvent was removed from the filtrate under reduced pressure. The residue was extracted with dry chloroform to give the phenol (II; *n* = 3) (0·98 g., 69%), m. p. and mixed m. p. 42° [light petroleum (b. p. 60—80°)].

N-(2-*Hydroxyethylato*)*salicylideneaminatocopper*(II) (III; *n* = 2).—Aqueous sodium hydroxide (40%; 8 ml.) was added to a mixture of the chelate (I; *n* = 2) (3·22 g.), cupric acetate (2·2 g.), ethanol (60 ml.), and water (10 ml.) to give the *chelate* (3·48 g., 94%), m. p. 259° (from dioxan) (Found: C, 48·7; H, 5·2; Cu, 20·1; N, 5·0. $C_9H_9CuNO_2\cdot C_4H_8O_2$ requires C, 49·6; H, 5·4; Cu, 20·2; N, 4·5%).

When the chelate (4·00 g.) was refluxed with ethylenediaminetetra-acetic acid (5·2 g.) in methanol (40 ml.) for 1 hr. the phenol (II; $n = 2$) was obtained in 47% yield.

N-(2-*Hydroxypropylato*)*salicylideneaminatocopper*(II) (V*a*).—This *chelate* was obtained in 83% yield as bluish-green plates, m. p. 256° (from dioxan), when a mixture of the chelate (IV*a*) (2·10 g.), cupric acetate (1·27 g.), ethanol (35 ml.), and water (3 ml.) was treated with sodium hydroxide (0·4 g.) in water (3 ml.) (Found: C, 50·2; H, 5·0; Cu, 25·2; N, 5·7. $C_{10}H_{11}CuNO_2$ requires C, 49·9; H, 4·6; Cu, 26·4; N, 5·8%).

N-2-(1-*Hydroxypropylato*)*salicylideneaminatocopper*(II) (V*b*) *and* N-2-(1-*Hydroxypropyl*)-*salicylideneamine* (VI*b*).—Bis(salicylaldehydato)copper(II) (1·53 g.) and 2-aminopropan-1-ol [11] (0·75 g.) were shaken in benzene (20 ml.) for 30 min., and the mixture was filtered to give the *chelate* (1·28 g., 99%), m. p. 157—158° (from dioxan) (Found: C, 52·1; H, 6·0; Cu, 19·0; N, 4·1. $C_{10}H_{11}CuNO_2,C_4H_8O_2$ requires C, 51·1; H, 5·8; Cu, 19·3; N, 4·3%). The solvent was removed from the filtrate under reduced pressure and the residue was extracted with hot light petroleum (b. p. 60—80°; 4 × 10 ml.) to give the *phenol* (462 mg., 52%), b. p. 127°/0·6 mm., n_D^{22} 1·5784 (Found: C, 67·2; H, 7·3; N, 7·7. $C_{10}H_{13}NO_2$ requires C, 67·0; H, 7·3; N, 7·8%).

N-2-(1-*Hydroxy*-2-*methylpropylato*)*salicylideaminatocopper*(II) (V*c*) *and* N-2-(1-*Hydroxy*-2-*methylpropyl*)*salicylideneamine* (VI*c*).—Bis(salicylaldehydato)copper(II) (3·06 g.) and 2-amino-2-methylpropan-1-ol (1·78 g.) were shaken in ethanol (40 ml.) for 20 min. The mixture was filtered to give the *chelate* (2·41 g., 95%), which crystallised from dioxan as bluish-green needles, m. p. 298—299° (Found: C, 52·6; H, 5·8; Cu, 19·1; N, 4·6. $C_{11}H_{13}CuNO_2,C_4H_8O_2$ requires C, 52·6; H, 6·2; Cu, 18·5; N, 4·1%). The solvent was removed from the filtrate under reduced pressure and the residue was dissolved in benzene (10 ml.). The solution was filtered through a short column of silica gel and concentrated under reduced pressure to give the *phenol* (0·93 g., 64%) as yellow needles, m. p. 63°, after crystallisation from light petroleum (b. p. 80—100°) (Found: C, 68·5; H, 7·8; N, 7·2. $C_{11}H_{15}NO_2$ requires C, 68·4; H, 7·8; N, 7·25%).

N-2-(1-*Hydroxy*-1-*phenylpropylato*)*salicylideneaminatocopper*(II) (V*d*) and N-2-(1-*Hydroxy*-1-*phenylpropyl*)*salicylideneamine* (VI*d*).—Bis(salicylaldehydato)copper(II) (10·50 g.) was condensed with 2-amino-1-phenylpropan-1-ol (5·21 g.) in benzene (40 ml.) in the usual manner to give salicylaldehyde (2·24 g., 53%), b. p. 100°/20 mm., and the *chelate* (10·2 g., 93%) as a bluish-grey solid, m. p. 216—218° (from benzene) (Found: C, 59·95; H, 4·9; Cu, 19·9; N, 4·6. $C_{16}H_{15}CuNO_2$ requires C, 60·0; H, 4·9; Cu, 20·4; N, 4·5%). The chelate (5·2 g.) was refluxed with ethylenediaminetetra-acetic acid (4·7 g.) in methanol (80 ml.) for 4 hr. to give the *phenol* as a very viscous yellow liquid, b. p. 210—220°(bath)/0·5 mm., which slowly crystallised and then had m. p. 64° (Found: C, 75·1; H, 6·5; N, 5·6. $C_{16}H_{17}NO_2$ requires C, 75·3; H, 6·7; N, 5·5%).

Preparation and Hydrolysis of Bis-[N-(2-*acetoxyethyl*)*salicylideneaminato*]*copper*(II) (IX*a*).—Bis(salicylaldehydato)copper(II) (3·06 g.), 2-acetoxyethylamine hydrochloride [12] (2·80 g.), and anhydrous sodium acetate (2·0 g.) were warmed in ethanol (40 ml.) for 5 min. The hot mixture was filtered and the filtrate was cooled to give the *chelate* (3·86 g., 81%), m. p. 140—141° (from ethanol) (Found: C, 55·5; H, 5·1; Cu, 13·6; N, 6·0. $C_{22}H_{24}CuN_2O_6$ requires C, 55·5; H, 5·1; Cu, 13·4; N, 5·9%).

The chelate (3·00 g.) was refluxed in a mixture of dioxan (160 ml.) and water (40 ml.) for 24 hr. The solution was concentrated under reduced pressure to a volume of about 20 ml. and then filtered to give the chelate (III; $n = 2$) (1·34 g., 93%) which was identified by its i.r. spectrum. The filtrate was fractionated to give *N*-acetylethanolamine (322 mg., 50%), b. p. 130°/0·4 mm., which was identical (i.r.) with an authentic sample.[3]

2-*Benzoyloxy*-1,1-*dimethylethylamine*.—2-Amino-2-methylpropan-1-ol (10 g.) and benzoyl chloride (15·8 ml.) were refluxed for 48 hr. in dry chloroform (100 ml.) which had previously been saturated with hydrogen chloride. The solvent was removed under reduced pressure and the residue was extracted with dry ether and recrystallised from ethanol to give the amino-ester hydrochloride (7 g., 27%) as needles, m. p. 224—225°. The hydrochloride (7 g.) was added to a saturated solution of ammonia in chloroform (70 ml.) and the mixture was filtered. The filtrate was fractionated to give the free *base* (4·27 g., 73%), b. p. 98—100°/0·6 mm., n_D^{20} 1·5123 (Found: C, 68·3; H, 8·0; N, 7·4. $C_{11}H_{15}NO_2$ requires C, 68·4; H, 7·8; N, 7·2%).

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Preparation and Reactions of Bis-[N-2-(1-*benzoyloxy-2-methylpropyl*)*salicylideneaminato*]-*copper*(II) (IX*b*).—(*a*) The preceding base (1·93 g.) and bis(salicylaldehydato)copper(II) (1·53 g.) were shaken in benzene (30 ml.) for 3½ hr., and the solvent was removed under reduced pressure. The residue was recrystallised from ether (20 ml.) to give the *chelate* (2·18 g., 67%), m. p. 148—150° (from ether) (Found: C, 65·8; H, 5·6; Cu, 9·7; N, 4·1. $C_{36}H_{36}CuN_2O_6$ requires C, 65·9; H, 5·5; Cu, 9·7; N, 4·3%).

(*b*) The chelate (960 mg.) was refluxed in a mixture of dioxan (40 ml.) and water (10 ml.) for 1½ hr. The mixture was concentrated under reduced pressure to a volume of about 10 ml., and then cooled and filtered to give the chelate (V*c*) (363 mg., 92%), m. p. 282—283°, which was identified by its i.r. spectrum. The solvent was removed from the filtrate under reduced pressure and the residue was extracted with ether (3 × 10 ml.). The extract was shaken with saturated aqueous sodium hydrogen carbonate (20 ml.), and the aqueous layer was separated and acidified with 10N-hydrochloric acid to give benzoic acid (140 mg., 78%), m. p. and mixed m. p. 120—121°. The ether layer was dried ($MgSO_4$) and fractionated to give *N-2-(1-benzoyloxy-2-methylpropyl)salicylideneamine* (X*b*) (421 mg., 95%) as a yellow liquid, b. p. 183°/0·6 mm., n_D^{20} 1·5675 (Found: C, 73·1; H, 6·1; N, 4·7. $C_{18}H_{19}NO_3$ requires C, 72·7; H, 6·4; N, 4·7%).

(*c*) The chelate (1·31 g.) was added to refluxing ethanol (100 ml.) to give a red solution which rapidly became green. The solution was refluxed for 2 min. and then quickly concentrated under reduced pressure to a volume of about 10 ml., and filtered to give the chelate (V*c*) (443 mg., 82%), m. p. 280—282°. The solvent was removed from the filtrate and the residue was extracted with hot light petroleum (b. p. 40—60°, 5 × 10 ml.). The extract was fractionated to give ethyl benzoate (196 mg., 66%), b. p. 78—80°/1 mm., and the phenol (X*b*) (467 mg., 79%), b. p. 180—186°/0·6 mm. The i.r. spectra of the three products were identical with those of authentic samples.

Reactions of Bis-[N-(2-*methoxyphenyl*)*salicylideneaminato*]*copper*(II) (XIII; R = H).—The chelate [13] (2·00 g.) was refluxed in dimethylformamide (100 ml.) for 24 hr. The mixture was cooled, diluted with water (100 ml.), and filtered to give the chelate (XV) (296 mg., 79% based on recovered starting material), which had an infrared spectrum identical with that of an authentic sample.[7] The filtrate was extracted with chloroform to give unchanged starting material (1·30 g., 65% recovery).

When the experiment was repeated on the same scale with refluxing chlorobenzene and with dimethyl sulphoxide at 200° as the solvents, the yields of the chelate (and recovered starting material) were 80 mg. (1·70 g.), and 256 mg. (1·10 g.), respectively.

Preparation and Reactions of Bis-[N-(2-*benzyloxyphenyl*)*salicylideneaminato*]*copper*(II) (XIII; R = Ph).—Salicylaldehyde (0·61 g.) and 2-benzyloxyaniline [14] (0·99 g.) were warmed in ethanol (5 ml.). Hot light petroleum (b. p. 80—100°; 20 ml.) was added and the mixture was cooled to give N-(2-*benzyloxyphenyl*)*salicylideneamine* (XIV; R = Ph) (1·25 g., 83%), as yellow needles, m. p. 79—80° (Found: C, 79·1; H, 5·7; N, 4·7. $C_{20}H_{17}NO_2$ requires C, 79·2; H, 5·65; N, 4·6%). This phenol (6·06 g.) in ethanol (20 ml.) was treated with aqueous cupric acetate (2·54 g. in 30 ml.) to give the copper *chelate* (6·20 g., 92%) which crystallised from benzene as plates, m. p. 173—174° (Found: C, 72·0; H, 5·0; Cu, 9·65; N, 4·3. $C_{40}H_{32}CuN_2O_4$ requires C, 71·9; H, 4·8; Cu, 9·5; N, 4·2%).

The chelate (1·134 g.) was refluxed in freshly distilled dimethylformamide (50 ml.) for 24 hr., and the mixture was concentrated under reduced pressure to a volume of about 20 ml. and filtered to give the chelate (XV) (300 mg., 64%). Ether (20 ml.) was added to the filtrate, and the mixture was cooled in ice and filtered to give unchanged starting material (39 mg., 3·5% recovery). The solvent was removed from the filtrate under reduced pressure, and the residue was crystallised from light petroleum (b. p. 80—100°) to give the phenol (XIV; R = Ph) (445 mg., 87%), m. p. 74—78°. In one experiment, the mother-liquors obtained after removal of the phenol were treated with α-naphthyl isocyanate (0·25 ml.) to give benzyl α-naphthylurethane (10 mg.), m. p. and mixed m. p. 134—136°.

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