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Macro Chelate Rings. III.[*1] Syntheses and Configurations of Complexes of New Ligands, 4,4′-Dimethyl-2,2′-bis(salicylideneaminomethyl)-diphenyl Ether and 4,4′-Dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine

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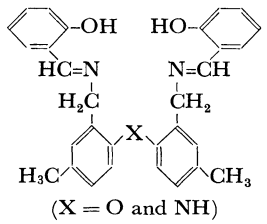
Two quadridentate chelating agents, 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenyl ether and 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine, which may form a metal complex with a ten-membered chelate ring, were synthesized by a sequence of steps. The cobalt(II), nickel(II), copper(II), and zinc(II) complexes could be derived from the ligands. Their configurations around the central divalent metal ion were explored on the basis of the absorption in the ligand field in a solution. A tetrahedral configuration for cobalt(II) complexes as well as the zinc(II) complexes, and a pseudo-tetrahedral configuration for the nickel(II) and copper(II) complexes, were concluded.

There have already been reports upon complexes derived from 2,7-dimethyl-4,5-bis(salicylideneaminomethyl)acridone[1)] and 2,7-dimethyl-4,5-bis(salicylideneaminomethyl)xanthone,[2)] which are sterically-controlled ligands and which form a non-planar metal complex with a ten-membered chelate ring with a divalent metal ion. They are rather favorable for a complex formation in that the two salicylideneaminomethyl groups are oriented in the same direction. If the carbonyl group in the acridone or the xanthone nucleus is eliminated from the ligand in each case, the new ligands thus made, which are 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine and 4,4′-dimethyl-2,2′-bis-(salicylideneaminomethyl)diphenyl ether (Fig. 1) respectively, may be quite flexible and may form a metal complex different from the complex of the parent ligands. Out of our interest in the configuration of the complex with a macro chelate ring, we attempted to prepare the new chelating agents 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenyl ether and 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine, shown in Fig. 1. It is, of course, one of the objects of this work to determine if a stable monomeric complex can be made from these ligands.



(X = O and NH)

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Fig. 1. Structures of the ligands.

X=O: 4,4′-Dimethyl-2,2′-bis(salicylideneaminomethyl)diphenyl ether

X=NH: 4,4′-Dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine

Experimental

Syntheses of Ligands. The synthetic schemes of the ligands are shown in Fig. 2. All the melting points are uncorrected.

2,2′-Dibromo-4,4′-dimethyldiphenyl Ether (II, X=O). To a solution of 4,4′-dimethyldiphenyl ether (40 g) in chloroform (100 m*l*), bromine (66.2 g) was added in the course of an hour's stirring, while the temperature was maintained at 60°C. The reaction mixture was then poured into water to give a pale-colored mass, which was collected and crystallized from alcohol as colorless prisms with a mp of 79—80°C. The yield was above 80%.

Found: C, 47.28; H, 3.51%. Calcd for $C_{14}H_{12}OBr_2$: C, 47.23; H, 3.68%.

2,2′-Dicyano-4,4′-dimethyldiphenyl Ether (III, X=O). A mixture of 2,2′-dibromo-4,4′-dimethyldiphenyl ether (30 g) and cuprous cyanide (15 g) in *N,N*-dimethylformamide (200 m*l*) was refluxed on an oil bath for six hours. Cuprous cyanide was then dissolved into a solution gradually. The reaction mixture was once filtered when hot and then poured into a hot solution of ferric chloride ($FeCl_3 \cdot 6H_2O$ 50 g, water 200 m*l*) to give a pale-colored mass of the nitrile, which

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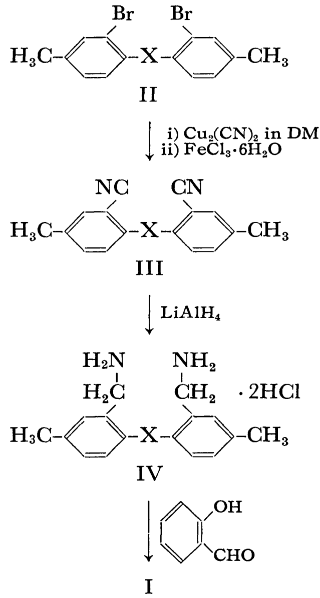
[*1] Part II: Ref. 2.

1) H. Okawa and T. Yoshino, This Bulletin, **42**, 1934 (1969).

2) H. Okawa and T. Yoshino, *ibid.*, **43**, 805 (1970).



(X=O and NH)

Fig. 2. The synthetic scheme of the ligands.

was collected, washed with water, and crystallized from ethanol as colorless needles with a mp of 131—132°C. The weight of the pure product was 16 g.

Found: C, 77.22; H, 4.77; N, 11.29%. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28%.

2,2′-Di(aminomethyl)-4,4′-dimethyldiphenyl Ether Dihydrochloride (IV, X=O). 2,2′-Dicyano-4,4′-dimethyldiphenyl ether (2.0 g) was reduced with lithium aluminum hydride (1 g) in tetrahydrofuran (50 m*l*). The mixture was then stirred for 5 hr at the boiling point of the solvent. After the reaction mixture had been decomposed with water (20 m*l*), the pH of the solution was adjusted to 8 and the inorganic substance which separated out was eliminated by filtration. The pale brown, oily substance which remained after the evaporation of the solvent was suspended in ether (150 m*l*), and to it we introduced a dry hydrogen chloride gas to give colorless needles of the diamine dihydrochloride. It was recrystallized from 95% ethanol.

Found: C, 58.31; H, 6.83; N, 8.33%. Calcd for $C_{16}H_{22}N_2OCl_2$: C, 58.26; H, 6.73; N, 8.51%.

4,4′-Dimethyl-2,2′-bis(salicylideneaminomethyl)-diphenyl Ether (I, X=O). 2,2′-Di(aminomethyl)-4,4′-dimethyldiphenyl ether dihydrochloride (0.6 g) and salicylaldehyde (1 g) were dissolved into 50% ethanol (150 m*l*), and then to the solution was added a 10% sodium bicarbonate solution until it was neutralized to give yellow needles; these needles were collected and recrystallized from ethanol as yellow needles with a mp of 92°C.

Found: C, 77.53; H, 6.03; N, 6.14%. Calcd for $C_{30}H_{28}N_2O_3$: C, 77.56; H, 6.08; N, 6.03%.

2, 2′-Dibromo-4, 4′-dimethyldiphenylamine (II, X=NH). To a solution of 4,4′-dimethyldiphenylamine (39.4 g) in chloroform (200 m*l*) we added bromine (35 g) over the course of one hour. After all of the bromine had been added, the stirring was continued for one more hour at the boiling point of chloroform. The reaction mixture was poured into water, and the organic layer was separated, washed with water, and dried over calcium chloride. When the solvent was evaporated, there remained an oily liquid, which soon solidified. It was crystallized from methanol as colorless needles with a mp of 61—63°C. The yield was 76%.

Found: C, 47.22; H, 3.66; N, 3.99%. Calcd for $C_{14}H_{13}NBr_2$: C, 47.36; H, 3.69; N, 3.94%.

2, 2′-Dicyano-4, 4′-dimethyldiphenylamine (III, X=NH). A solution of 2,2′-dibromo-4,4′-dimethyldiphenylamine (35.5 g) and cuprous cyanide (19.0 g) in *N,N*-dimethylformamide (200 m*l*) was heated on an oil bath for five hours. The reaction mixture was once filtered when hot, and then poured into a hot ferric chloride solution ($FeCl_3 \cdot 6H_2O$ 50 g, water 200 m*l*), to give a dark-colored, oily substance which solidified when cooled. It was collected, washed with water, and crystallized from methanol as colorless needles (17 g) with a mp of 151°C.

Found: C, 77.48; H, 5.26; N, 16.78%. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99%.

2,2′-Di(aminomethyl)-4,4′-dimethyldiphenylamine Dihydrochloride (IV, X=NH). To a solution of 2,2′-dicyano-4,4′-dimethyldiphenylamine (2 g) in tetrahydrofuran (50 m*l*), we added powdered lithium aluminum hydride (1 g). After the mixture had then been heated at the boiling point of the solvent for seven hours under stirring, the reaction mixture was decomposed with water and the pH of the solution was adjusted to 8. After any inorganic substances had been eliminated by filtration, the solvent was evaporated. There remained a viscous oily liquid. It was then treated in the same way as 2,2′-di(aminomethyl)-4,4′-dimethyldiphenyl ether, and the reduced product was isolated as dihydrochloride in the solid state. It was recrystallized from 95% ethanol as colorless needles.

Found: C, 55.83; H, 7.35; N, 12.36%. Calcd for $C_{16}H_{23}N_3Cl_2 \cdot H_2O$: C, 55.49; H, 7.28; N, 12.13%.

4,4′-Dimethyl-2,2′-bis(salicylideneaminomethyl)-diphenylamine (I, X=NH). To a solution of 2,2′-di(aminomethyl)-4,4′-dimethyldiphenylamine dihydrochloride (0.6 g) and salicylaldehyde (1 g) in 50% ethanol (150 m*l*), we added a 10% sodium bicarbonate solution until neutralization had been effected. A yellow precipitate which separated was collected and crystallized from ethanol as yellow prisms or needles with a mp of 130—131°C. The yield was quantitative.

Found: C, 77.70; H, 6.32; N, 8.97%. Calcd for $C_{30}H_{29}N_3O_2$: C, 77.73; H, 6.31; N, 9.06%.

Syntheses of Complexes. Cobalt(II), nickel(II), copper(II), and zinc(II) complexes could be made from the ligands. However, we were not successful in preparing palladium(II) and platinum(II) complexes. The methods of synthesizing the complexes were almost all the same; a typical procedure is given below. A slight excess of a metal acetate and a ligand (Schiff base) were treated in warm ethanol. The solution was kept at 60—70°C for about half an hour and then allowed to stand until its temperature went down to room temperature. The product which separated was collected and washed with a small amount of ethanol.

The cobalt(II) complexes are orange prisms, and the nickel(II) and copper(II) complexes were green and black prisms respectively. On the other hand, the zinc(II) complexes were almost colorless prisms. Although the molecular weights of these complexes are not

Table 1. Analyses of complexes*

		Found(%)				Calcd(%)			
		C	H	N	M	C	H	N	M
X=O	M=Co	68.80	4.98	5.57		69.10	5.03	5.37	
X=O	M=Ni	69.19	5.13	5.34		69.13	5.03	5.37	
X=O	M=Cu	67.25	5.07	5.41	12.23	67.35	5.09	5.24	11.87**
X=O	M=Zn	68.20	5.14	5.20		68.26	4.96	5.31	
X=NH	M=Co	69.33	5.39	8.09		69.25	5.23	8.07	
X=NH	M=Ni	69.05	5.42	7.96		69.26	5.23	8.08	
X=NH	M=Cu	68.38	5.17	7.83	11.86	68.62	5.18	8.00	12.10
X=NH	M=Zn	68.34	5.27	7.93		68.38	5.16	7.97	

* See Fig. 1 about X=O and X=NH.

** It contains a half molecule of water.

measured, they are surely monomeric. The results of elementary analyses of these complexes are given in Table 1.

Measurements. The electronic absorption spectra of the complexes in solution were determined with a Hitachi EPS-3T spectrophotometer in the near-infrared and visible regions at room temperature. Wako spectrograde pyridine was used in some measurements. The infrared spectra were measured with a Hitachi EPI-S2 spectophotometer in the region from 4000—650 cm^{-1} on a KBr disk.

Results and Discussion

Infrared Spectra of Complexes. Some main infrared absorption bands of complexes of 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenyl ether are given in Table 2. When a complex was formed, a red shift of from 10 to 25 cm^{-1} in the C=N stretching vibration was observed and a new absorption band appeared at 1535 cm^{-1}; this band being constant when the metal was changed. On the other hand, the C–O stretching vibration due to diphenyl ether did not appreciably shift upon complex formation; this demonstrates that the possibility of interaction as well as of bonding between the central metal ion and the oxygen in diphenyl ether can be eliminated and that the ligand acts as a quadridentate chelating agent, forming a metal complex with a ten-membered chelate ring.

Table 2. IR absorption bands of complexes of 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenyl ether(cm^{-1})

	C=N	New band	Ar–O–Ar	
Ligand	1635	—	1220	1250
M=Co	1612	1535	1228	1253
Ni	1610	1535	1225	1250
Cu	1620	1535	1225	1255
Zn	1625	1535	1225	1255

Table 3. IR absorption bands of complexes of 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine(cm^{-1})

	N-H	C=N	New band	C-N
Ligand	3400	1630	—	1310
M=Co	3325	1612	1535	1317
Ni	3350	1610	1535	1325
Cu	3370	1615	1535	1325
Zn	3325	1620	1535	1320

Data from the infrared absorption spectra of the complexes derived from 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine are given in Table 3. By a complex formation, a red shift by 10 to 20 cm^{-1} in the C=N stretching vibration was found and a new absorption band appeared at 1535 cm^{-1}; this band remained constant even when the metal was exchanged. Although the N–H stretching vibration shifted toward a lower wave number, the possibility of a direct interaction or bonding between the metal ion and the nitrogen atom in diphenylamine was also eliminated by the fact that the C–N stretching vibration of diphenylamine did not considerably shift upon complex formation. Thus, it can also be concluded that this compound is a quadridentate ligand which forms a complex with a ten-membered chelate ring.

The Electronic Absorption Spectra and Configurations of Complexes. The electronic absorption spectra of the cobalt(II) complex of 4, 4′-dimethyl-2, 2′-bis (salicylideneaminomethyl)diphenyl ether clearly showed that the configuration of the complex was always tetrahedral in chloroform as well as in pyridine (Fig. 3). As it is well known that a tetrahedral cobalt(II) complex, which is made from *N*-substituted salicylideneimine, changes to an octahedral complex in a donor solvent pyridine,[3] the steric condition of 4,4′-dimethyl-2,2′-

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[3] H. Nishikawa and S. Yamada, This Bulletin, **37**, 8 (1964); **38**, 1506 (1965); E. Yoshida and S. Yamada, *ibid.*, **40**, 1395 (1967).

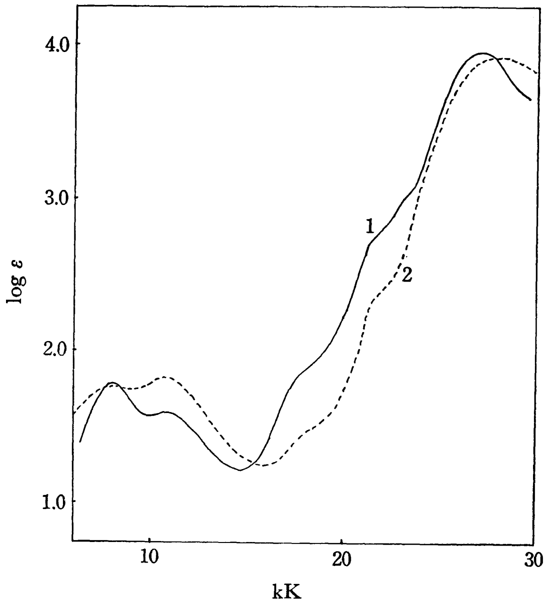

Fig. 3. Electronic absorption spectra of the cobalt(II) complex of 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenyl ether in chloroform (1) and pyridine(2).

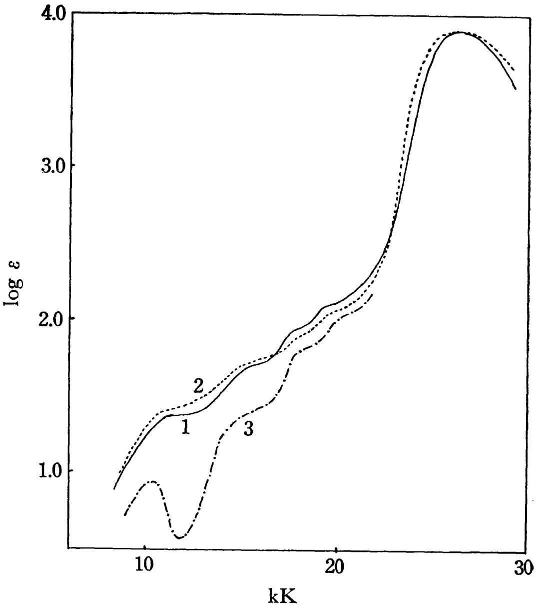

Fig. 4. Electronic absorption spectra of the nickel(II) complexes of 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenyl ether (1) and 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine (2) in pyridine, and bis(*N*-isopropylsalicylideneiminato)nickel(II) in chloroform (3).

bis(salicylideneaminomethyl)diphenyl ether may be quite unfavorable for an octahedral configuration around the cobalt(II) ion. On the other hand, the cobalt(II) complex of 4,4′-dimethyl-2,2′-bis-(salicylideneaminomethyl)diphenylamine was very unstable in solution, and we were unsuccessful in measuring the ligand-field band of the complex. However, it was supposed that the complex also had a tetrahedral structure because of the close resemblance of its infrared spectrum to that of the zinc(II) complex of 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine.

The ligand-field bands of the nickel(II) complexes were measured in pyridine. They are given in Fig. 4. The appearance of the d-d transition bands in the region from 10—15 kK precluded a planar configuration around the nickel(II) ion, as it had been well established that a square-planar configurational nickel(II) complex of *N*-substituted salicylideneimine showed two d-d transition bands at 16—18 and 20—24 kK.[4] Although the measurements were done in pyridine, the possibility of an octahedral configuration around the nickel(II) ion could also be rejected; two d-d transition bands, at 9—10 and at 15—17 kK, were found in an octahedral nickel(II) complex of *N*-substituted salicylideneimines.[4,5] Judging from these facts and from the resemblance of the spectra of the nickel(II) complexes to that of a nearly tetrahedral nickel(II) complex bis(*N*-isopropylsalicylideneiminato)nickel-(II), in which the angle between the planes containing the coordinating atoms of the chelate group and the nickel(II) atom is 81°,[6] it is quite natural to say that these nickel(II) complexes possess a tetrahedral configuration. The small shift in the ligand-field bands of our complexes from bis(*N*-isopropylsalicylideneiminato)nickel(II) may be caused by a distortion of a configuration around the nickel(II) ion.

The electronic absorption spectra of the copper(II) complexes measured in chloroform are given in Fig. 5. The d–d transition bands of the complexes shifted toward a considerably lower wave number than with a normal square-planar copper(II) complex, which had a d–d transition band at 17.5—17.7 kK. As it has been well established that this shift is caused by the distortion of the configuration around the copper(II) ion from coplanarity,[7] our complexes can be effected to be fairly much distorted. Yamada and Nishikawa[8] measured

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[4] S. Yamada, A. Takeuchi, K. Yamanouchi and K. Iwasaki, This Bulletin, **42**, 131 (1969).

[5] S. Yamada and K. Yamanouchi, *ibid.*, **42**, 2562 (1969).

[6] M. R. Fox, E. C. Lingafelter, P. L. Orioli and L. Sacconi, *Nature*, **197**, 1104 (1963).

[7] M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, **40**, 27 (1957); R. L. Belford and T. S. Piper, *Mol. Phys.*, **5**, 251 (1962).

[8] S. Yamada and H. Nishikawa, This Bulletin, **36**, 755 (1963).

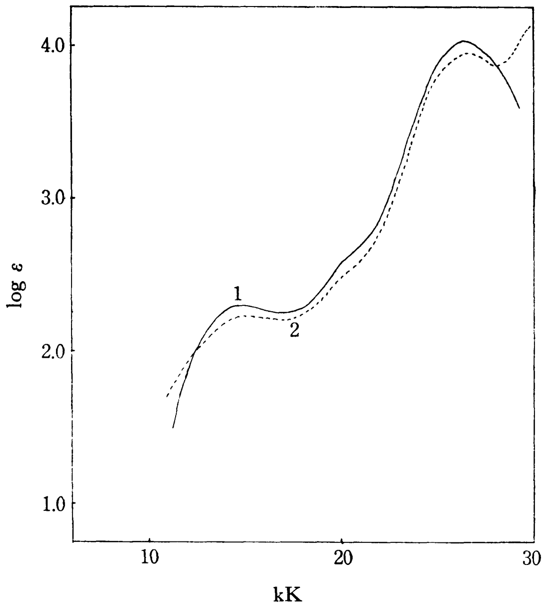

Fig. 5. Electronic absorption spectra of the copper(II) complexes of 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenyl ether (1) and 4,4′-dimethyl-2,2′-bis(salicylideneaminomethyl)diphenylamine (2) in chloroform.

the ligand-field bands of copper(II) complexes of *N*-R-substituted salicylideneimines in chloroform and found a band at 13 kK for R=*t*-butyl and one at 15.7 kK for R=isopropyl, *s*-butyl, 1-ethylpropyl or cyclohexyl; They decided that all of these are not planar but tetrahedral. On the other hand, Cheesemann *et al.*[9] studied several copper(II) complexes by X-ray analyses and found that the angle between the planes containing the coordinating atoms in the ligand and the central copper(II) ion in bis(*N*-*t*-butylsalicylideneiminato)copper(II) was only 54°. They also found that the angle in bis(*N*-ethylsalicylideneiminato)copper(II), which had been thought, from its absorption spectrum in solution, to be a planar complex, was unexpectedly, 36°. The drastic red shift in the d-d transition was, thus, caused by the fact that the angle between the planes containing the coordinating atoms and the central copper atom altered by only 18°. As the copper(II) complexes in this work had a ligand-field band at 14.7 kK, they must have an intermediate configuration. Insofar as their spectra are concerned, it is, however, reasonable to interpret the copper(II) complexes as exhibiting a pseudo-tetrahedral configuration.

The zinc(II) complexes must also have a tetrahedral configuration, judging from the steric requirements of the ligands, which inhibit a square-planar configuration, as well as from the tendency for a zinc(II) ion to take a tetrahedral configuration.

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[9] T. P. Cheesemann, D. Hall and T. N. Waters, *J. Chem. Soc.*, **1966**, 694.