Structure of Three-coordinated Copper(II) Complexes. Salicylalsalicylaminecopper(II) and Related Compounds

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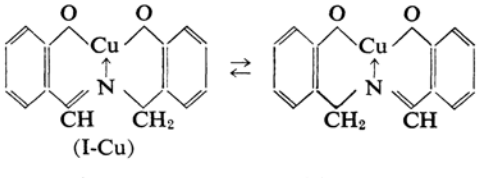
A majority of the so-called three-coordinated copper(II) complexes show magnetic moments per copper atom smaller than the theoretical spin moment, 1.73 Bohr magnetons, for one unpaired electron.[1] On the basis of this fact, the present writers predicted that the crystals of these compounds are made up of dimeric molecules having a pair of contiguous copper atoms close enough to permit spin interaction between them. The prediction was varified by an X-ray crystal analysis carried out by Barclay and collaborators[2] on a single crystal of acetylacetonemono(*o*-hydroxyanil)copper(II). It is noteworthy that the three-coordinated copper(II) complexes of this type were presumed to have monomeric units with a planar structure because they involve highly conjugated systems. In fact, the X-ray crystal analysis mentioned above confirmed this presumption. Therefore, one might suspect that the planar structure of ligands is an important factor leading to the subnormal magnetic moments of these copper(II) complexes. This generalization seems to be plausible because subnormal magnetic moments found for various copper(II) complexes[2,3] are a result of close proximity of two copper atoms in a dimeric molecule and the geometric configuration of ligands is surely responsible for the approach of the two copper atoms.

There is another group of three-coordinated copper(II) complexes, which show normal magnetic moments of 1.8—1.9 B. M.[4] Complexes belonging to this group are characterized by the presence of a six-membered chelate ring having a nonplanar structure in a monomeric molecule. Arguments based on infrared spectroscopy have led to a conclusion that complexes of this type also form dimeric molecules in crystals, in which copper atoms are bridged in pairs by two Cu-O-C-O-Cu links rather than by two oxygen atoms as in the copper(II) complexes of the first group. Thus, one is led to an important conclusion that "three-coordinated copper(II) complexes" in the literal sense of the word do not exist.[5]

Salicylalsalicylaminecopper(II) or salicylal-*o*-hydroxybenzylaminecopper(II) presents a single exception to this rule. It shows a subnormal magnetic moment of 0.87 B. M. at room temperature notwithstanding that a copper atom of this complex takes part in the formation of a six-membered ring having only one aromatic bond. However, the chemical formula as given to this molecule is based on the synthesis of the corresponding Schiff base. When the copper(II) complex is formed, one half of the monomeric unit might become equivalent to the other half, leading to a symmetric planar structure. It is because prototropic rearrangement involving slight displacements of three hydrogen atoms might take place.



(I-Cu)

For this reason, the problem of possible prototropy in this compound is important in discussing the structure of three-coordinated

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[1] M. Kishita, Y. Muto and M. Kubo, *Australian J. Chem.*, **10**, 386 (1957).

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

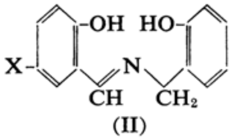
[3] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

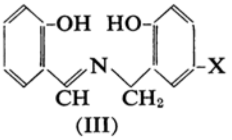
[4] M. Kishita, Y. Muto and M. Kubo, *Australian J. Chem.*, **11**, 309 (1958).

[5] M. Kubo, Y. Kuroda, M. Kishita and Y. Muto, ibid., **16**, 7 (1963).

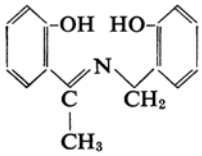
[6] M. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **74**, 261 (1953).

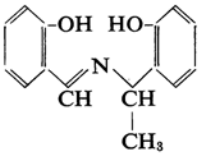
copper(II) complexes. The question can be answered by examining two derivatives of salicylalsalicylaminecopper(II), one having a substituent in the aldehyde portion of the Schiff base and the other having the same substituent at the corresponding position of the amine portion of the Schiff base. Yamaguchi⁶⁾ has already examined three isomeric pairs of Schiff bases which can form three-coordinated copper(II) complexes on replacing two hydrogen atoms with a copper atom. It is reported that no appreciable difference was found between the isomers in their ability to form coordination compounds but that those Schiff bases having a substituent on the aldehyde side show slightly lower melting points than those of the corresponding isomers having the same substituent on the amine side. (The three-coordinated copper(II) complexes have no sharp melting points, because they readily decompose before they melt.) Since the measurement of melting points alone is not very conclusive in deciding whether or not prototropy takes place in the molecules of this type, the present writers have undertaken to determine the infrared absorption spectra, the X-ray powder patterns, and the nuclear magnetic resonance spectra of salicylalsalicylamine and related compounds as well as their copper(II) salts.


(II)


(III)

X=Cl, NO_2


(V)



Experimental

The following Schiff bases and the corresponding three-coordinated copper(II) complexes were prepared by essentially the same method as that employed by Yamaguchi.⁶⁾

Salicylalsalicylamine (I).—This compound was prepared by the method described in a previous paper.¹⁾ It forms yellow needle crystals, m.p. 182°C. This and the following Schiff bases were transformed into their copper(II) salts by means of copper(II) acetate dissolved in ethanol. Recrystallization from pyridine yielded monopyridine adducts, which lost pyridine completely on boiling in ethanol.

Found: N, 5.0; Cu, 22.0. Calcd. for $C_{14}H_{11}O_2NCu$: N, 4.9; Cu, 22.0%.

5-Chlorosalicylalsalicylamine (II).—Salicylaldehyde was chlorinated with sulfuryl chloride in the presence of aluminum trichloride. 5-Chlorosalicylaldehyde separated as white crystals and was recrystallized from ethanol, m. p. 100°C. It was subjected to condensation with salicylamine in an ethanol solution. Recrystallization from ethanol yielded yellow needle crystals, m. p. 200°C.

Found: C, 63.8; H, 4.6; N, 5.3. Calcd. for $C_{14}H_{12}O_2NCl$: C, 64.2; H, 4.6; N, 5.3%.

Found: C, 52.5; H, 3.3; N, 4.4. Calcd. for $C_{14}H_{10}O_2NClCu$: C, 52.0; H, 3.1; N, 4.3%.

Salicylal-5-chlorosalicylamine (III).—*N*-(Hydroxymethyl)phthalimide was prepared by the reaction of phthalimide and formalin, m. p. 142°C. It was allowed to react with hydrochloric acid to obtain *N*-(chloromethyl)phthalimide, which was recrystallized from benzene, m. p. 132°C. On heating a mixture of this compound, *p*-chlorophenol, and zinc chloride, the reaction product solidified. Extraction with hot ethanol yielded white needle crystals of 2-hydroxy-5-chlorobenzylphthalimide, m. p. 171°C.⁷⁾ This compound was heated with hydrochloric acid in a sealed tube. On cooling, phthalic acid separated. When the filtrate was concentrated, 5-chlorosalicylamine hydrochloride precipitated. The precipitates were dissolved in water and neutralized with ammonia. The crystals of 5-chlorosalicylamine separated and were crystallized from ethanol, m. p. 204°C. This compound was allowed to condense with salicylaldehyde in an ethanol solution to form a Schiff base. Recrystallization from ethanol yielded yellow hexagonal plate crystals, m. p. 214°C.

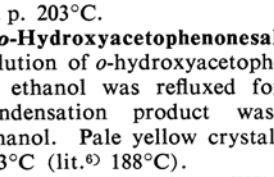
Found: C, 64.4; H, 4.5; N, 5.3. Calcd. for $C_{14}H_{12}O_2NCl$: C, 64.2; H, 4.6; N, 5.3%.

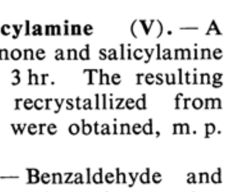
Found: C, 52.2; H, 3.2; N, 4.5. Calcd. for $C_{14}H_{10}O_2NClCu$: C, 52.0; H, 3.1; N, 4.3%.

5-Chlorosalicylal-5-chlorosalicylamine (IV).—This compound was obtained by the condensation of 5-chlorosalicylaldehyde and 5-chlorosalicylamine in an ethanol solution as yellow needle crystals, m. p. 203°C.

***o*-Hydroxyacetophenonesalicylamine (V).**—A solution of *o*-hydroxyacetophenone and salicylamine in ethanol was refluxed for 3 hr. The resulting condensation product was recrystallized from ethanol. Pale yellow crystals were obtained, m. p. 193°C (lit.⁶⁾ 188°C).

Benzalbenzylamine (VI).—Benzaldehyde and benzylamine were allowed to condense in an ether solution. After drying, ether was removed and the residue was fractionated under reduced pressure to obtain a colorless liquid, b. p. 140—145°C/5 mmHg (lit.⁸⁾ 200—202°C/10—20 mmHg).


(IV)


(VI)

Infrared absorpiton spectra were obtained of potassium bromide disks and Nujol mulls with a Model DS-402G grating spectrometer equipped with

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7) M. Yamaguchi, ibid., 73, 393 (1952).

8) A. T. Mason and G. R. Winder, *J. Chem. Soc.*, 65, 191 (1894).

potassium bromide optics from Japan Spectroscopic Company, Ltd. The wave number range covered 400—4000 cm^{-1}.

The X-ray powder patterns were taken by use of a Norelco X-ray diffractometer at room temperature with the copper Kα line filtered through nickel.

Nuclear magnetic resonance spectra were recorded at room temperature by means of a JNM-3 NMR spectrometer from the Japan Electron Optics Laboratory Company operating at 60 Mc. Materials were dissolved in dimethyl sulfoxide to 8—9% by weight unless otherwise specified. Cyclohexane was employed as an external standard.

Results and Discussion

A crucial test in this study is to see whether or not 5-chlorosalicylalsalicylamine (II) and its copper(II) salt (II-Cu) are identical with salicylal-5-chlorosalicylamine (III) and its copper(II) salt (III-Cu), respectively. If the prototropic rearrangement of hydrogen atoms takes place in the molecules of compound I and its derivatives, tautomeric equilibrium would be established between compounds II and III as well as between the salts, II-Cu and III-Cu. As a result, one would obtain one and the same Schiff base and its copper(II) salt regardless of whether chlorine is introduced in the aldehyde portion or the amine portion of compound I. For this reason, experimental results on related compounds are consulted below only when they are pertinent to the solution of the problem.

The infrared spectrum of compound II bears fairly close resemblance to that of III. However, there are certain features indicative of the nonidentity of the two compounds as shown in Fig. 1. The same conclusion can be derived from the spectra of three-coordinated copper(II) complexes, II-Cu and III-Cu, shown in Fig. 2. The assignments of observed bands are feasible to some extent on the basis of analysis carried out by Ueno and Martell⁹⁾ on a variety of metal chelates and free ligand molecules. However, the results are trivial for the present purpose and need not be discussed here.

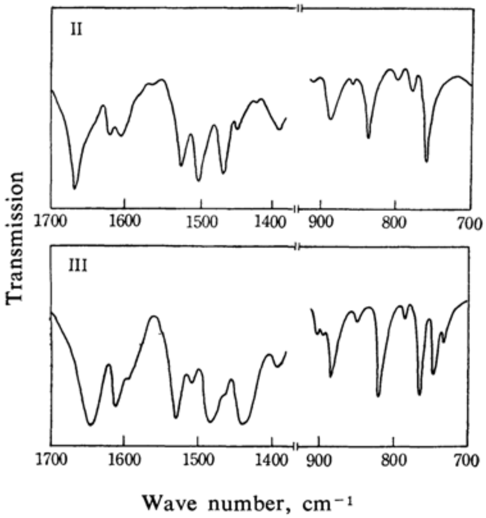

Fig. 1. Infrared spectra of 5-chlorosalicylalsalicylamine (II) and salicylal-5-chlorosalicylamine (III).

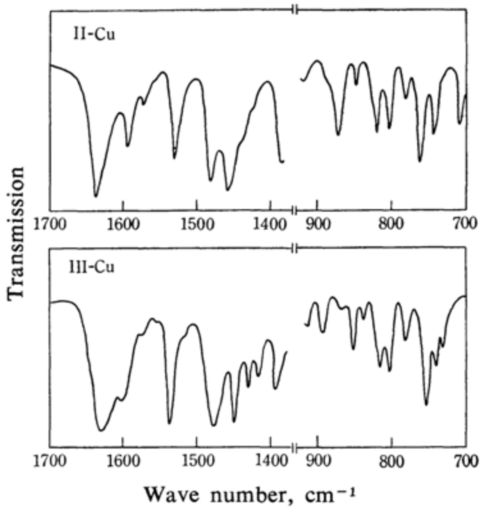

Fig. 2. Infrared spectra of 5-chlorosalicylalsalicylaminecopper(II) (II-Cu) and salicylal-5-chlorosalicylaminecopper(II) (III-Cu).

The X-ray powder patterns of free ligands, II and III, are quite different from each other (Fig. 3). The copper(II) salts of I, II, III, and IV also show powder patterns differing from one another as shown in Fig. 4.

It was not feasible to observe the nuclear magnetic reasonance spectra of the three-coordinated copper(II) complexes, because they are

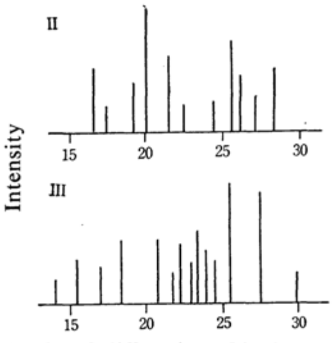

Fig. 3. Norelco X-ray powder patterns of 5-chlorosalicylalsalicylamine (II) and salicylal-5-chlorosalicylamine (III).

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9) K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955); **60**, 1270 (1956).

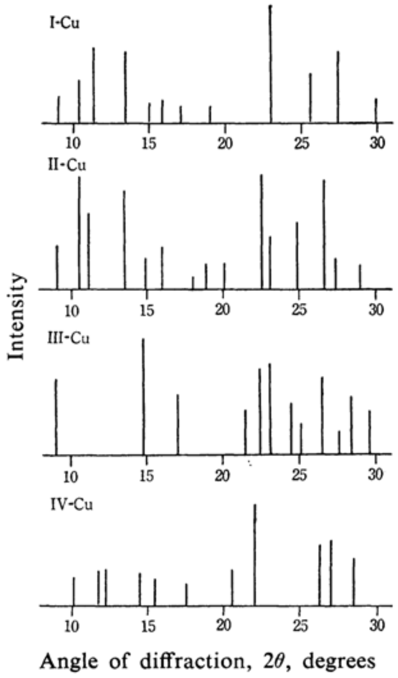

Fig. 4. Norelco X-ray powder patterns of the copper(II) complexes of salicylalsalicylamine (I-Cu), 5-chlorosalicylalsalicylamine (II-Cu), salicylal-5-chlorosalicylamine (III-Cu), and 5-chlorosalicylal-5-chlorosalicylamine (IV-Cu).

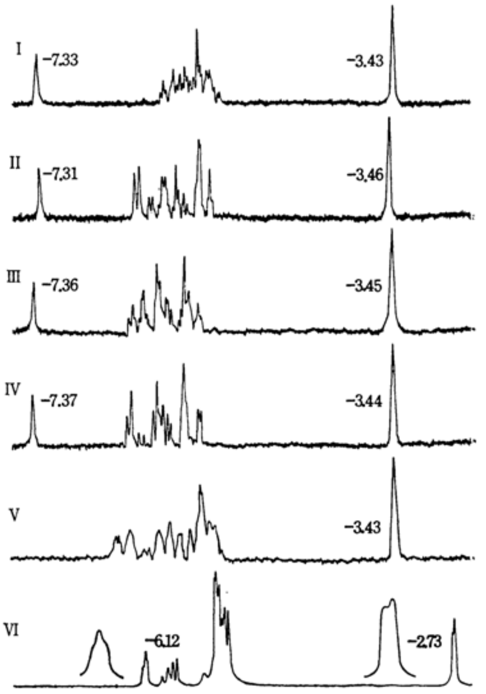

Fig. 5. Proton magnetic resonance spectra of salicylalsalicylamine (I) and related compounds (II—VI). The two peaks of compound VI as recorded in the pure liquid state show multiplet structure under a low sweep rate. They shift to low field when examined in solutions.

insoluble in almost all common solvents except pyridine, aniline, quinoline, etc. It is known that three-coordinated copper(II) complexes readily form monopyridine derivatives,[1,4] which show normal magnetic moments even when the corresponding pyridine-free complexes show subnormal magnetic moments. Accordingly, one is led to conclude that the dissolution of three-coordinated copper(II) complexes in pyridine involves the rearrangement of ligands and that the binuclear complex molecules dissociate into monomeric molecules each having a pyridine molecule as an additional ligand.[5] Undoubtedly, pyridine and other nitrogen-containing solvents are not suitable for the study of the structure of three-coordinated copper(II) complexes.

Therefore, proton magnetic resonance studies were made on free ligands, which also are sparingly soluble in a majority of common solvents. Internal standards were not employed, solely because it was desired to maintain the samples free from admixtures. No correction was made for the bulk magnetic susceptibility, because comparison between the NMR spectra of various compounds rather than the exact data of chemical shifts was the present writers' immediate concern.

The proton magnetic resonance spectra of compounds I—VI are shown in Fig. 5. The spectra of compounds I—IV look very much alike. Each consists of a sharp peak on the low-field side, a more intense sharp peak on the high-field side, and a group of closely spaced lines located between them. The intensity ratio of the two single lines is 1 : 2. Accordingly, the weak line is attributable to $-CH=$ protons while the strong line is due to $-CH_2-$ protons. The group of lines can be assigned to protons attached to aromatic rings. The signal of $-CH=$ protons is missing in the spectrum of compound V, which has $-C(CH_3)=$ in place of $-CH=$. The methyl signal of this compound was unobservable, because it overlaps the strong peak of dimethyl sulfoxide used as a solvent. The spectrum of compound VI also is comprised of a $-CH=$ proton signal, a $-CH_2-$ signal, and a group of peaks due to protons in phenyl groups. Since this compound could be examined in the pure liquid state, it was feasible to detect the multiplet structure of the $-CH=$ and $-CH_2-$ signals. The former signal has a line contour of a partly resolved 1 : 2 : 1 triplet while the latter shows a doublet structure. This indicates the existence of weak coupling between the $-CH=$

proton and -CH_2- protons. The signals of OH protons could not be observed, except for compound V for which a barely detectable flat peak was observed at -15.16—15.36 p.p.m. Probably, they are broadened by the intermolecular exchange of protons involving solvent molecules to escape detection. The results of assignments are summarized in Table I.

TABLE I. CHEMICAL SHIFTS (in p.p.m.) OF SALICYLALSALICYLAMINE (I) AND RELATED COMPOUNDS (II—VI) IN DIMETHYL SULFOXIDE SOLUTIONS WITH CYCLOHEXANE AS A STANDARD

Compound	-CH=	C_6H_3, C_6H_4, C_6H_5	-CH_2-
I	-7.33	-5.34—6.25	-3.43
II	-7.31	-5.39—6.30	-3.46
III	-7.36	-5.47—6.28	-3.45
IV	-7.37	-5.54—6.26	-3.44
V		-5.33—6.45	-3.43
VI (pure liq.)	-6.12	-5.23—5.96	-2.73

The appearance of two separate peaks for -CH= and -CH_2- protons provides a conclusive evidence for discarding possible prototropy in these molecules. As pointed out by Katritzky and Waring,[10,11] fast exchange can render two or more protons equivalent in a tautomeric compound and therefore the molecules simulate a more symmetric structure. In other words, if prototropy takes place in the molecules of salicylalsalicylamine and related compounds, one would have a single line for the -CH= and -CH_2- protons in contradiction with the present observations.

Conclusion

The experimental results described above indicate unequivocally that prototropy does not take place in the -CH=N-CH_2- portion of molecules of salicylalsalicylamine (I) and its derivatives as well as of the copper(II) salts derived from them. This fact has an interesting bearing on the structure of three-coordinated copper(II) complexes.

The so-called three-coordinated copper(II) complexes can be classified into two main groups. Those belonging to group I show subnormal magnetic moments, whereas group II complexes show normal magnetic moments. The latter differ from the former in two respects. First, a six-membered chelate ring having only one aromatic bond is present in a molecule (condition 1). The resulting nonplanar structure of the chelate ring might hinder the approach of two copper atoms. Secondly, complexes belonging to group II have a carbonyl group separated from a copper atom by two chemical bonds (condition 2), whereas a carbonyl oxygen capable of being coordinated on a copper atom of another monomeric molecule is missing in complexes classified as group I.

If one could prepare complexes having a three-dimensional configuration without any carbonyl oxygen and also those of a planar structure involving a carbonyl group at an appropriate position, it would be possible to decide which of the aforementioned two conditions is the main factor leading to normal magnetic moments. Quite recently, the present writers have succeeded in preparing salicylaldehydeglycinecopper(II), which satisfies condition 2 but not condition 1 and found that it shows a subnormal magnetic moment.[12] Salicylalsalicylaminecopper(II) studied in the present investigation satisfies condition 1 but not condition 2, since the double bond in the -CH=N-CH_2- portion of the molecule is localized. It shows a subnormal magnetic moment.[1] Thus, it is concluded that both of the aforementioned two conditions are necessary for three-coordinated copper(II) complexes to form a binuclear structure in which two copper atoms are bridged in a pair by two Cu-O-C-O-Cu links, whereas when either one or both of the two conditions are dissatisfied, dimeric complex molecules are formed, in which two copper atoms are bridged in a pair by two oxygen atoms.

Summary

On the basis of infrared spectroscopy and X-ray powder patterns, it is shown that 5-chlorosalicylalsalicylamine and its copper(II) salt are different from salicylal-5-chlorosalicylamine and its copper(II) salt, respectively, in the crystalline state. The nuclear magnetic resonance studies on salicylalsalicylamine and related compounds in solutions show that the double bond in the -CH=N-CH_2- portion of these molecules is localized, i. e., the prototropic rearrangement of hydrogen atoms does not take place. Therefore, salicylalsalicylaminecopper(II) presents an example of a new type of three-coordinated copper(II) complexes showing a subnormal magnetic moment in spite of having ligands of a three-dimensional structure. This provides an additional evidence in favor of a presumption made by the present writers on the structure of three-coordinated copper(II) complexes showing a normal magnetic moment.

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[10] A. R. Katritzky and A. J. Waring, *Chem. & Ind.*, **1962**, 695.

[11] W. G. Schneider, "Hydrogen Bonding," Ed. by D. Hadži, Pergamon Press, London (1959), p. 67.

[12] M. Kishita, A. Nakahara and M. Kubo, *Australian J. Chem.*, **17**, 810 (1964).

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