Metal Complexes with Terdentate Ligands. I. Synthesis of Copper(II) and Nickel(II) Complexes having Salicylaldehydesemicarbazone and Related Compounds as Ligands

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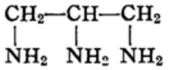
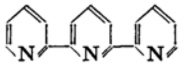
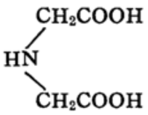
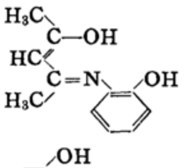
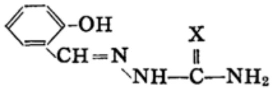
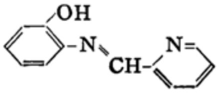
In marked contrast with the extensive studies that have been carried out on the metal complexes with terdentate ligands, those with terdentate ligands have received much less attention. The latters are of particular interest in coordination chemistry because of their steric requirements. A few examples of the terdentate chelating agents of types I and II are shown in Table I. The chelating agents of type III, while satisfying one primary valence of the metal, fill three coordination positions. The examples of type III are comparatively meagre.

It has been reported that a thiosemicarbazide molecule occupies two coordination positions of platinum(II)[1], palladium (II)[1], cobalt(II)[2], copper(II)[2] and nickel[2] ions* and that some thiosemicarbazones coordinate to copper(II)- and nickel ions as a bidentate ligand[3]. Semicarbazide forms complexes having the compositions, $CH_5ON_3CuCl_2$ and $(CH_5ON_3)_2NiSO_4$[4]. It is likely that a semicarbazide molecule occupies two coordination positions of copper(II) and nickel. Therefore, it is expected that semicarbazone or thiosemicarbazone of salicylaldehyde acts as a terdentate ligand of type II (in enol form) or type III (in keto form) and that α-pyridylaldehyde-*o*-hydroxyanil similarly acts as a ligand of type III. The present author synthesized copper(II) and nickel complexes having the ligands shown in Table II.

Salicylaldehydesemicarbazone was treated with copper(II) salts in a boiling ethanol solution. Depending on the kind of copper(II) salt, the copper(II) complexes of two different types were formed in the following way.

From the chemical analysis and the properties of the complex as well as the terdentate nature of the ligand, it seems reasonable to give the formula A to salicylaldehydesemicarbazone copper(II), although no direct evidence has yet been afforded by physical methods such as X-ray analysis. Similarly, the formula B has been presumed for salicylaldehydesemi-

TABLE I

Types	Example	
I. A-A-A[a)]	 $CH_2-CH-CH_2$ (each with NH_2)	
II. HA-A-AH[b)]		
III. HA-A-A	 (X: O, S.)	

a) A: a donor atom such as N, O and S. b) H: a hydrogen atom replaceable with metal atom. c) the enol form of acetylacetonemono-(2-hydroxyanil). Y. Muto, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **76**, 1407 (1955).

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[1] K. A. Jensen, *Z. anorg. allgem. Chem.*, **221**, 6 (1934).

[2] K. A. Jensen and E. Ranke-Madsen, ibid., **219**, 243 (1934).

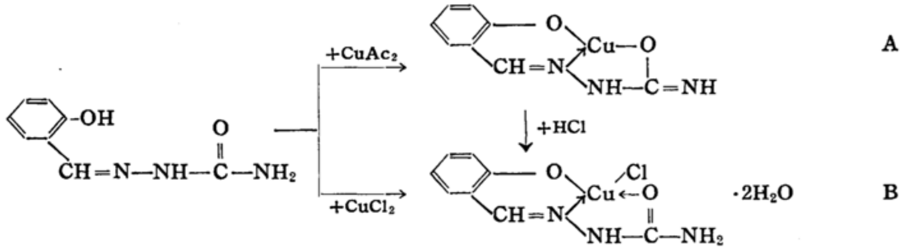
[3] G. Bähr and E. Hess, ibid., **268**, 351 (1952).

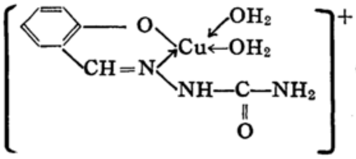
[4] K. A. Jensen and E. Ranke-Madsen, ibid., **227**, 25 (1936).

TABLE II

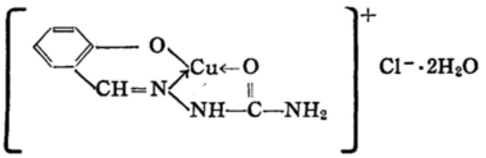
	Chelating agents (A)*	Composition of the complex	Solubility of the complex
1.	Salicylaldehydesemicarbazone	Cu(A)	Insol. in H_2O, EtOH, benzene. Sol. in pyridine.
		Cu(A)NH_3	Insol. in H_2O, benzene. Sol. in EtOH.
		Cu(A)Cl·$2H_2O$	Insol. in EtOH, benzene. Sol. in H_2O.
		Cu(A)NO_3	the same as the above
		$Ni(A)_2 \cdot H_2O$	Insol. in H_2O, EtOH, benzene, pyridine.
2.	5-Bromosalicylaldehydesemicarbazone	Cu(A)	Insol. in H_2O, EtOH, benzene.
		Cu(A)Cl	Insol. in EtOH, benzene. Slightly sol. in H_2O.
3.	Salicylaldehydethiosemicarbazone	Cu(A)	Insol. in H_2O, EtOH, benzene. Sol. in pyridine.
		Cu(A)py	Insol. in H_2O. Slightly sol. in EtOH.
		Cu(A)Cl·H_2O	Insol. in EtOH, benzene. Slightly sol. in H_2O.
		Ni(A)py	Insol. in H_2O. Slightly sol. in EtOH.
		$Ni(A)_2 \cdot 2H_2O$	Insol. in H_2O, EtOH, benzene. Sol. in pyridine.
4.	*α*-Pyridylaldehyde-*o*-hydroxyanil	Cu(A)Cl·$2H_2O$	Sol. in H_2O, EtOH, $CHCl_3$, nitrobenzene.
		Cu(A)$NO_3 \cdot 2H_2O$	the same as the above

* " A " denotes a terdentate ligand.





C



D

carbazone-monochloro copper(II) dihydrate for the following reasons. First, if salicylaldehydesemicarbazone were assumed to act as a bidentate ligand for a copper(II) ion, the chelate compounds with the molar ratio 1:2 of copper(II) to the reagent molecule should be formed just as in the case of Shiff's base prepared from salicylaldehyde and various primary amines. However, the composition of this complex and other copper(II) complexes obtained in this work had the molar ratio 1:1 of copper(II) to the reagent molecule as shown in Table II. Therefore, this reagent must occupy three coordination positions of a copper (II) ion. Secondly, from the fact that the water molecules contained in this complex could easily be removed by drying in a desiccator over calcium chloride at room temperature, it seems very likely that the water molecules do not coordinate directly to the copper atom. Thirdly, provided that the coordination number of copper(II) is four as usual, another unidentate ligand is required to fill the inner sphere around the copper atom which has already a terdentate ligand combined with it. Furthermore, the electric conductivity of dilute aqueous solutions of this complex was found to be small. Therefore, the chlorine atom is considered as being in the inner sphere around the copper atom, and it seems unlikely that this complex has a salt-like structure as shown in the formula C or D.

Experimental

1) **Salicylaldehydesemicarbazone copper (II).**—A solution of copper acetate monohydrate (0.6 g.) in water (30 ml.) was added to a boiling solution of salicylaldehydesemicarbazone (0.55 g.) in ethanol (50 ml.). Pale green micro crystals immediately precipitated. This precipitate was purified in the following way. The precipitate was dissolved in a mixture of ethanol (20 ml.) and aqueous ammonia (28%, 2 ml.) and then 10 ml. of water was added to it. The greenish solution was allowed to cool at room temperature for about three hours; mean while the addition compound with ammonia crystallized in gray prismatic crystals. The separated crystal was heated at 60~70°C until ammonia was no longer evolved. To ensure the complete removal of ammonia, the residue was boiled in ethanol on a water bath for ten minutes. After being allowed to cool, the precipitate was filtered off and dried at about 80°C.

Anal. Found: C, 39.92; H, 2.93; N, 17.46; Cu, 26.38%. Calcd. for $C_8H_7O_2N_3Cu$: C, 40.01; H, 3.15; N, 17.36; Cu, 26.19%.

The addition compound with ammonia liberates ammonia gradually at room temperature; hence the analysis was performed without delay after preparation.

Anal. Found: N, 21.70; Cu, 24.69; NH_3, 6.44%. Calcd. for $C_8H_7O_2N_3Cu \cdot NH_3$: N, 21.74; Cu, 24.65; NH_3, 6.61%.

2) **Salicylaldehydesemicarbazone - mono chloro copper(II) dihydrate.**—A hot solution of copper(II) chloride dihydrate (0.5 g.) in water (10 ml.) was added to a hot solution of salicylaldehydesemicarbazone (0.5 g.) in ethanol (20 ml.). The greenish solution was allowed to stand overnight at room temperature. The green precipitate formed was washed with ethanol. The pure compound was obtained in deep green prismatic crystals by recrystallization from water. The hydrate lost water gradually in a desiccator over calcium chloride and was completely dry at 50~60°C. The color of the crystals became brown after dehydration.

Anal. Found: C, 30.77; H, 3.79; N, 13.73; Cl, 11.23; Cu, 20.34; H_2O, 11.40%. Calcd. for $C_8H_8O_2N_3ClCu \cdot 2H_2O$: C, 30.68; H, 3.94; N, 13.70; Cl, 11.32; Cu, 20.29; H_2O, 11.50%.

This compound was also obtained by heating the compound prepared in 1) with dilute hydrochloric acid on a water bath.

3) **Salicylaldehydesemicarbazone - mononitrato copper(II).**—This compound was prepared in the same way as the monochloro compound by the reaction between salicylaldehydesemicarbazone and copper(II) nitrate. The green crystals formed were dried in a desiccator over calcium chloride at room temperature.

Anal. Found: N, 18.51; Cu, 20.77%. Calcd. for $C_8H_8O_5N_4Cu$: N, 18.45; Cu, 20.92%.

4) **Bis-salicylaldehydesemicarbazone nickel monohydrate.**—A solution of nickel acetate tetrahydrate (0.5 g.) in water (10 ml.) was added to a boiling solution of salicylaldehydesemicarbazone (0.7 g.) in ethanol (40 ml.). Light green prismatic crystals were immediately precipitated. The separated crystals were washed with hot ethanol, then with pyridine and finally with hot water and they were dried in a vacuum desiccator. The corresponding nickel complex was not formed by the reaction between nickel sulfate and salicylaldehydesemicarbazone although the solutions were mixed in the same way as described above.

Anal. Found: N, 19.31; Ni, 13.7%. Calcd. for $C_{16}H_{16}O_4N_6Ni \cdot H_2O$: N, 19.41; Ni, 13.6%.

5) **5-Bromosalicylaldehydesemicarbazone copper(II).**—This compound was prepared as pale green micro crystals in the same way as the compound described in 1).

Anal. Found: N, 13.38; Cu, 19.92%. Calcd. for $C_8H_6O_2N_3BrCu$: N, 13.15; Cu, 19.88%.

6) **5-Bromosalicylaldehydesemicarbazone-monochloro copper (II).**—This compound was prepared in the same way as the compound described in 2). The gray crystals formed were dried in a desiccator over calcium chloride at room temperature.

Anal. Found: N, 11.86; Cu, 17.80%. Calcd. for $C_8H_7O_2N_3ClBrCu$: N, 11.80; Cu, 17.84%.

7) **Salicylaldehydethiosemicarbazone copper(II).**[5]—This compound was prepared in the same way as the compound described in 1). The brown crystals formed were dried at 60°C.

Anal. Found: C, 37.62; H, 3.10; N, 16.41; Cu, 24.74%. Calcd. for $C_8H_7ON_3SCu$: C, 37.42; H, 2.75; N, 16.36; Cu, 24.75%.

The pyridinate of this copper complex was obtained as pale brown needles by recrystallizing it from pyridine.

Anal. Found: N, 16.71; Cu, 19.02; pyridine, 23.49%. Calcd. for $C_8H_7ON_3SCu \cdot C_5H_5N$: N, 16.68; Cu, 18.92; pyridine, 23.55%.

8) **Salicylaldehydethiosemicarbazone-monochloro copper(II) monohydrate.**—This compound was prepared in the same way as the

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[5] V. Hovorka and Z. Holzbecher, *Collection Gzechoslov. Chem. Communs.*, **15**, 267 (1950).

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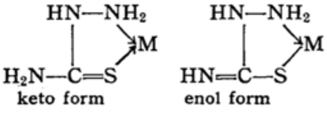

keto form enol form

M: bivalent metal.

compound described in 2). Green prismatic crystals.

Anal. Found: N, 13.68; Cu, 20.23%. Calcd. for $C_8H_8ON_3SClCu \cdot H_2O$: N, 13.50; Cu, 20.41%.

9) **Monopyridino-salicylaldehydethiosemicarbazone nickel.**—A solution of nickel acetate tetrahydrate (0.5 g.) in water (10 ml.) was added to a boiling solution of salicylaldehydethiosemicarbazone (0.4 g.) in ethanol (30 ml.). Orange crystals were precipitated immediately. The separated precipitate was dissolved in pyridine and filtered. When water was added to the filtrate, the monopyridino compound separated out as brown-red needles.

Anal. Found: N, 16.92; Ni, 17.6; pyridine, 23.12%. Calcd. for $C_8H_7ON_3SNi \cdot C_5H_5N$: N, 16.93; Ni, 17.7; pyridine, 23.90%.

10) **Bis-salicylaldehydethiosemicarbazone nickel dihydrate.**—A hot solution of nickel sulfate heptahydrate (0.3 g.) in water (5 ml.) was added to a boiling solution of salicylaldehydethiosemicarbazone (0.4 g.) in ethanol (50 ml.). Light green crystals were precipitated immediately. The separated precipitate was boiled in ethanol on a water bath, filtered off and washed by hot water. This procedure was repeated two or three times, and then the crystals were dried in a vacuum desiccator.

Anal. Found: N, 17.67; Ni, 12.08%. Calcd. for $C_{16}H_{16}O_2N_6S_2Ni \cdot 2H_2O$: N, 17.40; Ni, 12.10%.

When this compound was recrystallized from pyridine, the monopyridino compound described in 9) was formed.

11) **α - Pyridylaldehyde - *o* - hydroxyanil-monochloro copper (II) dihydrate.** — This compound was prepared in the same way as the compound described in 2) by the reaction between copper(II) chloride and α-pyridylaldehyde-*o*-hydroxyanil. Brown-black prismatic crystals.

Anal. Found: C, 43.70; H, 4.00; N, 8.22; Cu, 19.07; H_2O, 10.80%. Calcd. for $C_{12}H_9ON_2ClCu \cdot 2H_2O$: C, 43.40; H, 3.95; N, 8.44; Cu, 19.12; H_2O, 10.84%.

12) **α - Pyridylaldehyde - *o* - hydroxyanil-mononitrato copper (II) dihydrate.** — This compound was prepared in the same way as the compound described in 2) by the reaction between copper nitrate and α-pyridylaldehyde-*o*-hydroxyanil. Brown-black prismatic crystals.

Anal. Found: N, 11.60; Cu, 17.63; H_2O, 10.01%. Calcd. for $C_{12}H_9O_4N_3Cu \cdot 2H_2O$: N, 11.71; Cu, 17.71; H_2O, 10.04%.

13) **Electric conductance of copper (II) complexes.**—The concentration of the solution used for measurement at 15°C was 0.001 M. The results were listed in Table III.

TABLE III

	Compound	Molar conductance (mho)
1.	Salicylaldehydesemicarbazone -monochloro copper(II) dihydrate	30.5
2.	Salicylaldehydesemicarbazone -mononitrato copper(II)	32.5
3.	α-Pyridylaldehyde-*o*-hydroxyanil -monochloro copper(II) dihydrate	30.7
4.	α-Pyridylaldehyde-*o*-hydroxyanil -mononitrato copper(II) dihydrate	30.5

The pH values of these solutions were found to be 5.4∼6.3. Therefore, it is possible that these complexes decompose to some extent in water. This accounts for such a low yield as 50% of the recrystallization of these complexes from water.

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