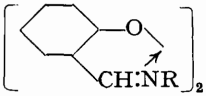
422. *Co-ordinated Copper and Nickel Compounds of Salicylidene Derivatives.*

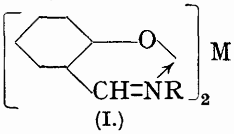
By Louis Hunter and John A. Marriott.

Copper and nickel compounds of the type



M (where R = Ar, NHAr, $NH{\cdot}CO{\cdot}NH_2$) and also nickel salicylaldazine are described. Their solubilities and other properties are consistent with the co-ordination indicated in the formula. None of the copper derivatives offers any advantage over that of salicylaldoxime for the determination of copper.

Apart from the well-known metallic complexes derived from salicylaldoxime (Ephraim, *Ber.*, 1930, **63**, 1928; Brady, J., 1931, 105) no comprehensive study has been made of the tendency of compounds of formula $(o)HO{\cdot}C_6H_4{\cdot}CH{:}NR$ to form chelate metallic salts. That this tendency is quite general is proved by the preparation and properties of copper and nickel complexes of general formula (I) derived from salicylidene-amines (R = aryl), -arylhydrazones (R = -NHAr), -semicarbazones (R = $-NH{\cdot}CO{\cdot}NH_2$), and -azines. None of the salts described offers any advantage over cupric salicylaldoxime as a means of gravimetric estimation of copper.



(I.)

The properties of the metallic derivatives described below leave no doubt as to their co-ordinated structure. They are crystalline substances, usually having a definite melting point, are decomposed by acid but stable to alkali, insoluble in water, sparingly soluble in alcohol but readily in benzene, nitrobenzene, chloroform, and pyridine. An important conclusion to be drawn from the general tendency of the salicylidene derivatives to form chelate metallic salts is that the configuration of the aryl groups about the $-CH{:}N-$ is *trans*, for without this arrangement six-membered ring formation involving the metal is impossible. This conclusion is in harmony with the results of Hendricks, Wulf, Hilbert, and Liddel (*J. Amer. Chem. Soc.*, 1936, **58**, 1991), who, from the absence of bands typical of the hydroxyl group from the absorption spectra of salicylidene-aniline, -hydrazone, and -phenylhydrazone and salicylaldazine, deduce that the *o*-hydroxyl hydrogen is co-ordinated to nitrogen, necessarily implying a *trans*-configuration. Support for a chelated (and therefore a *trans*-) structure for the salicylidene-amines is also obtained from their superior solubility in organic solvents and their invariably lower melting points, as compared with the *m*- and *p*-isomers. Suppression of the usual associating function of the hydroxyl group was observed in salicylideneaniline, the molecular weight of which in benzene solution remained virtually normal over a considerable range of concentration.

Since its discovery by Ettling (*Annalen*, 1840, **35**, 241), the copper salt derived from hydrosalicylamide has been the subject of much discussion. By analogy with similar compounds, Delépine (*Bull. Soc. chim.*, 1899, **21**, 943) considered it to be derived from the unknown salicylaldimine, and this is now confirmed for both copper and nickel salts by molecular-weight determinations. The molecular weights of salts possessing a hydrosalicylamide structure would be almost three times those actually found.

By analogy with the metallic derivatives of the salicylidenediamines described by Pfeiffer and his co-workers (*Annalen*, 1933, **503**, 84; *J. pr. Chem.*, 1936, **145**, 243), double formulæ (*i.e.*, two metal atoms per molecule) have been ascribed to *nickel disalicylidenebenzidine* and *nickel salicylaldazine*.

Experimental.

(All temperatures are corrected.)

Two general methods are available for the preparation of the copper and nickel salts described below.

1. *By the action of metal acetate on the salicylidene derivative.* To the salicylidene derivative (2 mols.) in hot alcohol is slowly added a solution of the metal acetate (1 mol.) in 50% aqueous alcohol. The copper complexes are usually precipitated at once in a crystalline condition, but the nickel complexes frequently require the addition of alkali to neutralise the liberated acetic acid. This is best accomplished by adding slightly less than the theoretical amount of sodium hydroxide dissolved in alcohol; ammonia, especially in excess, must be avoided, as it leads to the formation of the metal derivative of salicylaldimine. After standing until the mixture is cold, the precipitated complex is filtered off and washed with water and alcohol; it is then usually pure enough for analysis.

2. *By the action of metal acetate on a mixture of salicylaldehyde and the amine or the hydrazine derivative.* To the amine or the hydrazine (2 mols., or 1 mol. of a diamine) in hot alcohol is added a hot alcoholic solution of salicylaldehyde (2 mols.), and a solution of the metal acetate (1 mol.) in 50% aqueous alcohol is added as before. If the salicylidene derivative is insoluble in alcohol, the salicylaldehyde may be added to a mixture of the amine and metal acetate; or the salicylaldehyde and metal acetate solutions may be added alternately, a few c.c. at a time, to the amine solution.

Estimation of the salicylidene residue. A convenient check on the composition of some of the metal complexes was provided by the estimation of the salicylidene residue ($-O{\cdot}C_6H_4{\cdot}CH{=}$, indicated in the subsequent analyses as "Sal."). This was performed gravimetrically by converting the salicylaldehyde obtained from them by the action of acid into salicylaldazine as follows. A weighed quantity (0·03—0·05 g.) of the metallic complex is decomposed by 50% sulphuric acid (25 c.c.), and the liberated salicylaldehyde driven over in steam into an alkaline solution of hydrazine. The operation is conveniently carried out in a micro-Kjeldahl distillation apparatus. The salicylaldazine is then precipitated by the addition of acid, and collected in a small (8 c.c.) sintered-glass crucible, washed with dilute acid and water, and finally dried in a vacuum desiccator. Under these conditions the solubility of the azine is less than 1 mg./l., and the error due to this cause need not exceed 0·1 mg. of salicylaldazine (*i.e.*, about 0·2%). Weight of salicylidene residue = 0·875 × weight of azine.

The following compounds were obtained.

*Cupric salicylidene-*o*-toluidine*, dark brown, shining rhombic plates, m. p. 243—246° (decomp.) (Found : N, 5·9; Cu, 13·3. $C_{28}H_{24}O_2N_2Cu$ requires N, 5·8; Cu, 13·1%); m-*isomer*, brown rhombic plates with a red reflex, m. p. 188° (decomp.) (Found : N, 5·6; Cu, 13·1%); p-*isomer*, shining brown rhombic plates, m. p. 211—213° (decomp.) (Found : N, 5·8; Cu, 13·2%).

Cupric salicylidene-α-naphthylamine, small, brown, rectangular plates from chloroform, m. p. 259° (decomp.) (Found : N, 5·0; Cu, 11·6. $C_{34}H_{24}O_2N_2Cu$ requires N, 5·0; Cu, 11·4%); β-*compound*, thin, irregular, hexagonal plates from chloroform, m. p. 194—196° (Found : N, 5·0; Cu, 11·6%).

*Cupric salicylidene-*m*-chloroaniline*, microcrystalline, red-brown powder, m. p. 210—212° (decomp.) (Found : N, 5·2; Cu, 12·2. $C_{26}H_{18}O_2N_2Cl_2Cu$ requires N, 5·3; Cu, 12·1%); p-*compound*, chocolate-brown, microcrystalline powder, appearing as brown rhombic plates when precipitated from chloroform solution by addition of ether, m. p. 240° (Found : N, 5·4; Cu, 12·3%).

*Cupric salicylidene-*p*-bromoaniline*, red-brown, microcrystalline powder, appearing as golden-brown, rhombic plates when precipitated from chloroform solution by light petroleum; m. p. 250—251° (Found : N, 4·8; Cu, 10·3. $C_{26}H_{18}O_2N_2Br_2Cu$ requires N, 4·6; Cu, 10·4%).

*Cupric salicylidene-*m*-nitroaniline*, yellow, microcrystalline powder, m. p. 272° (decomp.) after blackening at 229° (Found : N, 10·2; Cu, 11·6. $C_{26}H_{18}O_6N_4Cu$ requires N, 10·3; Cu, 11·65%); p-*compound*, red-brown, microcrystalline powder, but clusters of needles when precipitated from pyridine by light petroleum; m. p. 313° (decomp.) after blackening at 308° (Found : N, 10·2; Cu, 11·8%).

*Cupric salicylidene-*o*-anisidine*, brown, microcrystalline powder, m. p. 222° (decomp.) (Found : N, 5·5; Cu, 12·6. $C_{28}H_{24}O_4N_2Cu$ requires N, 5·4; Cu, 12·3%); p-*compound*, red-brown, microcrystalline powder, m. p. 179° (decomp.) after blackening at 169° (Found : N, 5·6; Cu, 12·3%); when precipitated from chloroform solution by addition of ether, these compounds formed dark brown cubic crystals and rhombic plates, respectively.

Cupric salicylaldimine, prepared from hydrosalicylamide or from salicylaldehyde in the presence of ammonia, formed a green crystalline powder, m. p. 195° (decomp.) [Found : N, 9·2; Cu, 21·2; *M* (Rast), 290. $C_{14}H_{12}O_2N_2Cu$ requires N, 9·2; Cu, 20·9%; *M*, 304]; it appears to be identical with the copper " salicylimide " described by Ettling (*loc. cit.*).

Cupric salicylidenehydrazone, light brown powder, decomposing at 270—275° without melting (Found : Cu, 19·0; Sal., 63·8. $C_{14}H_{14}O_2N_4Cu$ requires Cu, 19·0; Sal., 63·0%); the corresponding *phenylhydrazone*, brown microcrystalline powder, m. p. 174° (Found : Cu, 13·3; Sal., 42·8. $C_{26}H_{22}O_2N_4Cu$ requires Cu, 13·1; Sal., 43·2%), when precipitated from chloroform solution by ether; and the p-*nitrophenylhydrazone*, microcrystalline brown powder, m. p. 221° (decomp.) (Found : Cu, 11·6. $C_{26}H_{20}O_6N_6Cu$ requires Cu, 11·3%).

Nickel salicylideneaniline, microcrystalline green powder, m. p. 248° (decomp.) (Found : N, 6·3; Ni, 12·9. $C_{26}H_{20}O_2N_2Ni$ requires N, 6·2; Ni, 13·0%); the corresponding derivatives of o-*toluidine*, green rhombic plates, m. p. 293° (decomp.) (Found : N, 5·9; Ni, 12·3. $C_{28}H_{24}O_2N_2Ni$ requires N, 5·9; Ni, 12·3%); m-*toluidine*, yellowish-green powder, appearing as small green rhombic plates when precipitated from chloroform solution by ether, m. p. 260° (Found : N, 5·8; Ni, 12·35%); p-*toluidine*, green octahedra from chloroform, m. p. 274° (decomp.) (Found : N, 5·7; Ni, 12·1%).

Nickel salicylidene-α-naphthylamine, green powder, m. p. 311° (decomp.) after blackening at 306° (Found : N, 5·2; Ni, 10·6. $C_{34}H_{24}O_2N_2Ni$ requires N, 5·1; Ni, 10·65%); β-*compound*, yellow powder, m. p. 220° after blackening at 206° (Found : N, 5·2; Ni, 10·4%); when precipitated from chloroform solution by addition of ether, these formed yellow needles and green rhombic plates, respectively.

*Nickel salicylidene-*o*-anisidine*, brown rhombic plates or rods, m. p. 319° (decomp.) (Found : N, 5·4; Ni, 11·3. $C_{28}H_{24}O_4N_2Ni$ requires N, 5·5; Ni, 11·5%). Nickel salicylaldimine, prepared from trisalicylidenediamine or from salicylaldehyde in the presence of ammonia, formed yellow rhombs with a golden reflex; when precipitated from dilute aqueous alcohol, the hydrate was obtained (Found : N, 8·9; Ni, 18·9. Calc. for $C_{14}H_{12}O_2N_2Ni,H_2O$: N, 8·9; Ni, 18·7%), but from acetone or from absolute alcohol the anhydrous complex, m. p. 335°

(decomp.) [Found: N, 9·2; Ni, 19·5; *M* (Rast), 308. Calc. for $C_{14}H_{12}O_2N_2Ni$: N, 9·3; Ni, 9·6%; *M*, 299], was obtained.

Nickel disalicylidenebenzidine, yellowish-green, microcrystalline powder, crystallising from pyridine in green rhombic plates, which do not melt or decompose below 360° (Found: N, 6·2; Ni, 12·9. $C_{52}H_{36}O_4N_4Ni_2$ requires N, 6·2; Ni, 13·1%).

Nickel salicylidenehydrazone, light brown powder, appearing as yellow microcrystals when precipitated from pyridine solution by alcohol; it decomposed without melting at 313° (Found: Ni, 17·4; Sal., 64·9 $C_{14}H_{14}O_2N_4Ni$ requires Ni, 17·8; Sal., 64·5%). *Phenylhydrazone* analogue, green rhombic plates from chloroform, decomposing indefinitely without melting at about 230° (Found: Ni, 12·0; Sal., 43·7. $C_{26}H_{22}O_2N_4Ni$ requires Ni, 12·2; Sal., 43·7%). *Nickel salicylaldazine*, light brown powder, stable without melting to 360° (Found: Ni, 19·5; Sal., 70·0. $C_{28}H_{20}O_4N_4Ni_2$ requires Ni, 19·8; Sal., 70·8%). *Nickel salicylidenesemicarbazone*, small, yellow, rhombic plates, decomposing at 302° (Found: Ni, 14·3; Sal., 50·9. $C_{16}H_{16}O_4N_6Ni$ requires Ni, 14·1; Sal., 50·6%).

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