49. *Compounds of Naphthoic Acids with their Copper and Nickel Salts. Copper and Nickel Sulphinates and their Oxidation to Sulphonates.*

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Copper and nickel salts of α- and β-naphthoic and α- and β-naphthalene- and *p*-toluene-sulphinic acids are described. The naphthoic acids form both acid and basic compounds, but the sulphinic acids form only normal salts. With the exception of nickel α-naphthalenesulphinate, the compounds of the α-acids are soluble in organic solvents, and those of the β-acids insoluble. In this respect they resemble the acid potassium compounds.

The oxidation of the sulphinates to the corresponding sulphonates is described, and the dehydration of the sulphonates is discussed.

A crystalline basic compound of copper β-naphthoate is described.

Copper and *nickel α-naphthoate* and *copper α-naphthalenesulphinate* are all soluble in organic solvents, whereas the corresponding *salts* of the β-acids are insoluble. In this respect they resemble the α- and β-acid potassium compounds, the former having the properties of an un-ionised compound, and the latter those of a salt (Wright, J., 1940, 859). It is notable, however, that all the copper salts have the strong green colour characteristic of co-ordinated copper, suggesting that this difference is not one of degree of ionisation. Since it exists in the copper compounds as well as in the acid potassium compounds, the difference in the latter case cannot be connected with the acidic hydrogen; *i.e.*, it is not due to the two molecules being connected, the α- by the potassium atom, causing chelation, and the β- by the hydrogen atom, leaving the potassium ionised.

With β-naphthoic acid, copper and nickel form both basic and acid *compounds*: β-$Cu(C_{10}H_7{\cdot}CO_2)_2,Cu(OH)_2$; 3β-$Cu(C_{10}H_7{\cdot}CO_2)_2,C_{10}H_7{\cdot}CO_2H$; 3β-$Ni(C_{10}H_7{\cdot}CO_2)_2,Ni(OH)_2$; β-$Ni(C_{10}H_7{\cdot}CO_2)_2,C_{10}H_7{\cdot}CO_2H,2H_2O$. With α-naphthoic acid, copper forms a basic and nickel an acidic *compound*: α-$Cu(C_{10}H_7{\cdot}CO_2)_2,Cu(OH)_2$; α-$Ni(C_{10}H_7{\cdot}CO_2)_2,C_{10}H_7{\cdot}CO_2H,2H_2O$. The acid salts of the β-acid are both formed by the action of acetone on the normal salt, the basic compounds being simultaneously precipitated. Basic nickel β-naphthoate is also formed by the action of other organic solvents on the normal salt, β-naphthoic acid being produced in solution. Basic copper β-naphthoate is soluble in aqueous ammonia and is deposited in deep blue prisms as the ammonia evaporates on exposure to air. Crystalline copper hydroxide has been prepared in this manner (Hayek, *Monatsh.*, 1936, **67**, 352).

The acid nickel salts of both α- and β-naphthoic acids melt at comparatively low temperatures. Both the hydrates and the dehydrated substances are soluble in organic solvents.

Copper and nickel sulphinates do not form either basic or acid compounds. The copper salts are characterised by a bright yellow colour which changes to green on hydration but is not regenerated when the hydrates are dried at 100°, the latter retaining their green colour and crystalline appearance.

Copper α-naphthalenesulphinate is highly hydrated. It slowly dissolves in cold water to form a pale blue solution, from which bright yellow, anhydrous flakes separate on heating, and very pale blue, almost colourless prisms of a hexahydrate separate at 0°. In this substance the brilliant colour of co-ordinated copper is markedly absent, and it seems likely that the copper ion is completely surrounded by water molecules. The hexahydrate loses all its water at 45°, becoming bright yellow. It is insoluble in organic solvents, but in contact with acetone or chloroform the crystals turn into the bright yellow anhydrous substance, and then dissolve, forming yellow solutions. In benzene the crystals remain unchanged and insoluble.

Separation of α- and β-Naphthoic Acids.—The solubility of the copper salt of the α-acid and the insolubility of that of the β-acid in alcohol provide a convenient method of separating the two acids when prepared from the mixed product of the sulphonation of naphthalene.

Identification of α- and β-Naphthalenesulphinic Acids.—The copper salts of both α- and β-naphthalenesulphinic acid are precipitated by adding copper nitrate to neutral solutions of the ammonium salts. As the β-compound is bright yellow when precipitated, and rapidly turns green on the filter, whereas the α-compound is precipitated as the almost white hexahydrate, this constitutes a method of distinguishing between the two acids, whose m. p.'s, 96° and 98°, are too near for identification purposes.

Oxidation of Sulphinates to Sulphonates in Alcoholic Solution.—The *p*-toluenesulphinates are readily oxidised to the corresponding sulphonates in alcohol. The bright yellow alcoholic solution of copper *p*-toluenesulphinate is immediately decolorised on evaporation in air, becoming strongly acid; the solution yields only crystals of the sulphonate. The nickel salt is oxidised when a current of air is passed through its suspension in boiling alcohol; after some hours a clear green solution is produced, which yields crystals of the pure *sulphonate*, no other substance being formed.

Copper β-naphthalenesulphinate is only partly oxidised to sulphonate by the latter process; other acid copper substances are produced, some copper oxide is precipitated, and a bright yellow oil formed. On addition of benzene to the concentrated alcoholic solution, however, a 50% yield of the sulphonate separates. Similar results are obtained with the nickel compound. Copper α-naphthalenesulphonate cannot be obtained from the sulphinate by this method, but the nickel sulphonate is formed so readily that it is the sole product of the action of nickel carbonate on α-naphthalenesulphinic acid in alcoholic solution, and constitutes about 50% of the product when the reaction takes place in ether.

Dehydration of Sulphonates—As the extensive hydration of the sulphonates has been discussed in connection with the maximum co-ordination number of copper, it is noteworthy that copper and nickel *p*-toluenesulphonate and copper β-naphthalenesulphonate lose only $4H_2O$ at 100°, falling into white powders. Since the acids themselves are monohydrates, the other two molecules of water are probably attached one to each acid radical. Moreover, α-naphthalenesulphonic acid, which is a dihydrate and cannot be dehydrated without decomposition (Fierz and Weissenbach, *Helv. Chim. Acta*, **1920**, **3**, 314), yields a copper salt which loses only $2H_2O$ at 100°.

EXPERIMENTAL.

Copper *p*-toluenesulphinate was described by Meyer (*J. pr. Chem.*, 1901, **63**, 171) as a pale green trihydrate. By the action of copper carbonate on *p*-toluenesulphinic acid in alcoholic solution, however, it was obtained as a yellow precipitate; this was sparingly soluble in boiling water, grass-green plates of the trihydrate separating from the boiling solution [Found: Cu, 14·7; loss at 100°, 12·7. Calc. for $Cu(C_7H_7\cdot SO_2)_2,3H_2O$: Cu, 14·9; $3H_2O$, 12·6%]. Pale green needles, also of the trihydrate (Found: Cu, 14·7; loss at 100°, 12·44%), separated from the cooled solution at 40°, and dark green needles of the *hemihydrate* separated from the cold solution on standing overnight [Found: C, 44·0; H, 4·1; Cu, 17·0; loss at 100°, 3·3. $Cu(C_7H_7\cdot SO_2)_2,\frac{1}{2}H_2O$ requires C, 43·9; H, 3·9; Cu, 16·6; $\frac{1}{2}H_2O$, 3·1%].

Copper *p*-toluenesulphonate and copper and nickel α- and β-naphthalenesulphonates have been described (*Ber.*, 1879, **12**, 1851; Fierz and Weissenbach, *loc. cit.*; Witt, *Ber.*, 1915, **48**, 755), but only for copper β-naphthalenesulphonate has the loss of water at lower temperatures than those required for complete dehydration been noted. Witt describes a loss of 4 mols. at 75—80°, and Fierz and Weissenbach only 2 mols. at 80°. The sulphonates prepared by oxidation of the sulphinates, and also from the sulphonic acids for verification, gave the following results: copper *p*-toluenesulphonate hexahydrate lost $4H_2O$ at 100°, forming a white powder (Found: loss, 14·06. Calc. for $4H_2O$: loss, 14·0%); on complete dehydration a green powder was produced (Found: loss at 240°, 20·9. Calc. for $6H_2O$: loss, 21·0%). Copper β-naphthalenesulphonate hexahydrate lost $4H_2O$ at 100°, falling into a white powder (Found: loss, 12·36. Calc. for $4H_2O$: loss, 12·3%). Nickel β-naphthalenesulphonate suffered no loss in weight at 100°. Copper α-naphthalenesulphonate hexahydrate lost $2H_2O$ at 100°, its crystalline appearance remaining unchanged, but its colour fading (Found: loss, 6·23. Calc. for $2H_2O$: loss, 6·14%); on complete dehydration the colour became bright orange, but the crystalline structure was undamaged (Found: loss at 185°, 18·2. Calc. for $6H_2O$: loss, 18·4%). Nickel α-naphthalenesulphonate hexahydrate lost $3H_2O$ at 100° and $4H_2O$ at 150°, and was completely dehydrated at 185°, its crystalline appearance remaining unchanged (Found: loss at 100°, 150°, and 185°, 9·3, 12·5, 18·9 respectively. Calc. for 3, 4, and $6H_2O$: loss, 9·3, 12·3, 18·6%, respectively).

Nickel Salts of Naphthoic Acids.—*Nickel α-naphthoate* was formed as a pale green precipitate by the action of nickel carbonate (0·75 g.) on α-naphthoic acid (3 g.) in alcohol (15 c.c.), some remaining in the alcohol. It crystallised from boiling water as a tetrahydrate in pale green prisms, soluble and stable in alcohol, acetone, ether, chloroform, and benzene [Found: Ni, 12·2; loss at 100°, 15·5. $Ni(C_{11}H_8O_2)_2,4H_2O$ requires Ni, 12·4; $4H_2O$, 15·2%]. The dehydrated substance showed the same solubilities and the salt separated in this form from the last three solvents.

Acid nickel α-naphthoate was formed together with the normal salt by the action of nickel carbonate (0·25 g.) on the acid (2 g.) in alcohol (15 c.c.) for 6 months; the acid salt was found in the alcoholic solution, and was purified by solution in acetone, from which it separated as a dihydrate in pale green prisms, m. p. 135° (decomp.) [Found: Ni, 9·2; loss at 100°, 5·9. $Ni(C_{11}H_8O_2)_2,C_{11}H_9O_2,2H_2O$ requires Ni, 9·6; $2H_2O$, 5·9%]. It was very soluble in alcohol, acetone, chloroform, benzene, and ether, separating from the last three as a glassy solid. When heated, it gave off α-naphthoic acid. The anhydrous substance showed the same solubilities.

Nickel β-*naphthoate* was formed when the acid (2 g.) and nickel carbonate (0·5 g.) were boiled together in water (20 c.c.) for 3 hours, pale green prisms of the trihydrate separating from the filtered solution at 0°. From boiling water this hydrate separated in flakes; it was also precipitated by the action of nickel nitrate solution on a neutral solution of the ammonium salt [Found: Ni, 13·07; loss at 150°, 12·06. $Ni(C_{11}H_8O_2)_2,3H_2O$ requires Ni, 12·9; $3H_2O$, 11·9%]. It was soluble in, but decomposed by, acetone, with the formation of an acid salt in solution and a basic precipitate; and decomposed by benzene, ether, or chloroform, to form a basic precipitate and β-naphthoic acid in solution.

Acid nickel β-*naphthoate* was formed by the action of acetone on nickel β-naphthoate crystals, the substance obtained from the acetone solution being repeatedly redissolved in small quantities of acetone until no residue formed on evaporation. The crystals of dihydrate produced were then completely soluble in acetone, ether, benzene, and chloroform and separated from the last three as a glassy solid, m. p. 148° (decomp.) [Found: Ni, 9·5; loss at 100°, 6·0. $Ni(C_{11}H_8O_2)_2,C_{11}H_9O_2,2H_2O$ requires Ni, 9·6; $2H_2O$, 5·9%]. The anhydrous substance showed the same solubilities.

Basic nickel β-*naphthoate* was formed as a pale green precipitate by the action of acetone on the normal salt. After drying at 100°, it was insoluble in water and all organic solvents [Found: Ni, 18·1. $3Ni(C_{11}H_8O_2)_2,Ni(OH)_2$ requires Ni, 18·1%].

Copper Salts of α-*Naphthoic Acid*.—(1) *Copper* α-*naphthoate monoalcoholate* (1·4 g.) was produced when α-naphthoic acid (1·3 g.) in alcohol (20 c.c.) and basic copper carbonate (1 g.) were boiled for 5 mins. and set aside for a week. It formed dark green needles containing 1 EtOH, and was recrystallised from alcohol containing the free acid [Found: Cu, 14·0; loss at 100°, 10·5. $(C_{11}H_7O_2)_2Cu,C_2H_6O$ requires Cu, 14·2; C_2H_6O, 10·2%]. These were very soluble in acetone, and from the solution dark green plates, containing 1 $COMe_2$, separated [Found: Cu, 13·8; loss at 100°, 12·6. $(C_{11}H_7O_2)_2Cu,C_3H_6O$ requires Cu, 13·8; C_3H_6O, 12·5%]; this *solvate* was insoluble in water, but soluble in ether, chloroform, benzene, carbon tetrachloride, alcohol, and acetone, decomposing in all these solvents except acetone to give the basic compound (see below). When heated until anhydrous, the crystals retained their colour and crystalline appearance.

(2) *Basic copper* α-*naphthoate* was precipitated when a solution of the normal salt in alcohol was boiled; after being washed with alcohol and acetone and dried at 100°, it formed a blue amorphous solid [Found: Cu, 25·1. $(C_{11}H_7O_2)_2Cu,Cu(OH)_2$ requires Cu, 25·4%], soluble in ammonia, from which it was deposited, on evaporation of the ammonia, as a dark blue, amorphous solid. It was insoluble in alcohol, water, and all organic solvents. On heating, it retained its blue colour until it charred.

Copper Salts of β-*Naphthoic Acid*.—(1) Copper β-naphthoate (0·9 g.) was produced as a Wedgewood-blue precipitate when a solution of the acid (0·75 g.) in alcohol (20 c.c.) was kept for 1 week in contact with basic copper carbonate (0·5 g.). After being dissolved in boiling acetone and filtered from the precipitated basic salt, it separated on cooling in prisms of the same colour, which were washed with alcohol [Found: Cu, 15·7. $(C_{11}H_7O_2)_2Cu$ requires Cu, 15·66%]. The same substance was precipitated from the acetone solution, in fine green needles, by addition of alcohol. It was slightly soluble in water, from which small, blue, anhydrous prisms were obtained on evaporation (Found: Cu, 15·8%), and was insoluble in all organic solvents, except acetone, which decomposed it into the insoluble basic compound (see below) and an acid substance which formed a deep blue solution in the acetone. On heating, the crystals kept their shape and lustre, but turned green.

(2) *Acid copper* β-*naphthoate*, of noteworthy composition, was formed when the normal salt was shaken with acetone at 35°, the solution filtered, and kept without evaporation overnight at 12°. Large peacock-blue prisms were formed, which when heated to 100° crumbled to powder but did not lose weight [Found: Cu, 13·5. $3(C_{11}H_7O_2)_2Cu,C_{11}H_8O_2$ requires Cu, 13·7%]. At higher temperatures β-naphthoic acid sublimed.

(3) *Basic copper* β-*naphthoate* was produced when a solution of the normal salt (1 g.) in acetone (150 c.c.) was refluxed until nearly colourless. The precipitate was boiled with fresh acetone, filtered off, washed with alcohol and ether, and dried at 100° [Found: Cu, 25·3. $(C_{11}H_7O_2)_2Cu,Cu(OH)_2$ requires Cu, 25·4%]. When this was dissolved in aqueous ammonia and set aside until the solution became colourless, it was regenerated as deep blue crystals (Found: Cu, 25·6%). The precipitated basic salt was a pale blue powder, insoluble in water and organic solvents; on heating, it retained its blue colour until it charred.

Nickel p-*toluenesulphinate* was formed as a pale cream precipitate when nickel carbonate (0·6 g.) was kept for a week in an alcoholic solution of the acid (3 g.); it was insoluble in alcohol, and very sparingly soluble in water, from which it separated in cream anhydrous flakes [Found: Ni, 16·0. $Ni(C_7H_7SO_2)_2$ requires Ni, 16·0%].

Nickel p-*toluenesulphonate* was formed when a current of air was passed through the above sulphinate, suspended in alcohol, until a clear, pale green solution was produced (*ca.* 6 hours). It was also prepared by the action of nickel carbonate on the sulphonic acid. It was very soluble in water, from which it separated in pale green needles of the *hexahydrate*. At 100° it lost $4H_2O$, crumbling to a white powder, and it became completely dehydrated at 180° [Found: Ni, 11·5; loss at 100°, 14·3, 14·4, 14·4; loss at 180°, 21·1. $Ni(C_7H_7{\cdot}SO_3)_2,6H_2O$ requires Ni, 11·5; $4H_2O$, 14·15; $6H_2O$, 21·2%].

Salts of α-*Naphthalenesulphinic Acid*.—(1) *Copper* α-*naphthalenesulphinate* was formed as a greenish-yellow precipitate by the action of copper carbonate (0·87 g.) on the acid (3 g.) in boiling alcohol or ether [Found:

Cu, 13·8. $Cu(C_{10}H_7{\cdot}SO_2)_2$ requires Cu, 14·2%]. It was soluble in cold water, from which it separated on boiling in bright yellow, crystalline flakes (Found : Cu, 13·8%). From the saturated solution at 0°, very pale blue prisms of a *hexahydrate* were deposited [Found : Cu, 11·2; loss at 45°, 19·4. $Cu(C_{10}H_7SO_2)_2,6H_2O$ requires Cu, 11·5; $6H_2O$, 19·5%]. This hydrate was also precipitated by addition of copper nitrate to a neutral solution of the ammonium salt of the acid.

(2) *Nickel α-naphthalenesulphinate dihydrate* was formed as a very pale cream precipitate by the action of nickel carbonate (0·69 g.) on the acid (2·4 g.) in boiling ether. The fine precipitate was separated by decantation, and freed from the sulphonate by thorough washing with water [Found: Ni, 12·3; loss at 100°, 7·6. $Ni(C_{10}H_7SO_2)_2,2H_2O$ requires Ni, 12·3; $2H_2O$, 7·55%]. It was soluble in boiling water, from which pale green plates of a *tetrahydrate* separated on evaporation [Found : Ni, 11·5; loss at 100°, 13·9. $Ni(C_{10}H_7SO_2)_2,4H_2O$ requires Ni, 11·45; $4H_2O$, 14·0%]; this was insoluble in alcohol and acetone.

Salts of β-Naphthalenesulphinic Acid.—(i) The *copper* salt was formed as a yellow precipitate by the action of copper carbonate (0·5 g.) on the acid (2 g.) in warm alcohol [Found : Cu, 14·1. $Cu(C_{10}H_7SO_2)_2$ requires Cu, 14·2%]. It was insoluble in organic solvents, very sparingly soluble in alcohol, and sparingly soluble in boiling water, from which it crystallised on cooling in bright green plates of a *dihydrate* [Found : Cu, 13·0; loss at 100°, 7·5. $Cu(C_{10}H_7SO_2)_2,2H_2O$ requires Cu, 13·2; $2H_2O$, 7·5%]. A bright yellow precipitate, rapidly turning into the green dihydrate on the filter, was obtained by addition of copper nitrate to a neutral solution of the ammonium salt of the acid. On dehydration the dihydrate retained its green colour.

(ii) The *nickel* salt was obtained as a pale green, granular precipitate by the action of nickel carbonate on excess of the acid in alcoholic solution, and was washed with alcohol and benzene [Found : Ni, 13·5. $Ni(C_{10}H_7SO_2)_2$ requires Ni, 13·3%]. It was insoluble in water, alcohol, and all organic solvents.

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