

**281. Complex Nickel Compounds. Part I. The Formation and Solvation of Nickalous Chloride in some Non-aqueous Liquids.**

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LITTLE is known of the reaction between nickel and hydrochloric acid; the dilute acid is stated to have very little effect (Hale and Foster, *J. Soc. Chem. Ind.*, 1915, **34**, 464), but there is no record of the reaction between the metal and solutions of hydrogen chloride in non-aqueous liquids. Various organic liquids of widely different structure have now been used as solvents for the hydrogen chloride, and it has been found possible to divide these liquids into three classes, *viz.*,

Group I.	Group II.	Group III.
Water	Ethyl ether	Chloroform
Methyl alcohol	Methyl acetate	Carbon tetrachloride
Ethyl alcohol	Ethyl acetate	Carbon disulphide
Propyl alcohol		Light petroleum
<i>iso</i> Propyl alcohol		Benzene
Acetic acid		Nitrobenzene

*Group I.*—Solutions of hydrogen chloride in these liquids attack nickel rapidly with evolution of heat, the nickalous chloride and the liquid forming a green or blue-green, soluble co-ordination compound. The rate of reaction increased with decreasing molecular weight of the solvent, and in water and the lower alcohols a yellowish-green precipitate of the co-ordination compound was soon formed. On the other hand, with the higher alcohols and acetic acid, the co-ordination compound was formed only after prolonged passage of hydrogen chloride.

*Group II.*—Solutions in these liquids attack nickel more slowly, forming brownish-green solutions of the co-ordination compound. In this case the compound was not precipitated from solution by continued action of the hydrogen chloride.

*Group III.*—Solutions in these liquids do not attack nickel.

The conditions of the reactions between iron and hydrogen chloride dissolved in various liquids have already been described (Chesterman, *J.*, 1935, 906), and it is interesting to compare those results with the present work. Apparently nickel is slightly less reactive than iron, since the only differences observed were with acetone and chloroform as solvents, for hydrogen chloride in these two liquids reacts with iron, but not with nickel.

In addition, three further liquids have been examined, *viz.*, nitrobenzene, acetic acid, and *n*-propyl alcohol. Since it has been shown (*loc. cit.*) that the chief factors affecting this type of reaction are (*a*) solubility of hydrogen chloride in the liquid and (*b*) specific conductivity of the saturated hydrogen chloride solution, which is a measure of the extent of ionisation of the hydrogen chloride, these values have now been determined, *S* being the solubility (grams of hydrogen chloride/gram of solution) under the given pressure, and  $\kappa$  the conductivity (mhos) of the saturated solution, both at 25° :

	Propyl alcohol.	Nitrobenzene.	Acetic acid.
S .....	0.313/768 mm.	0.00085/760 mm.	0.067/758 mm.
$\kappa$ .....	$1.71 \times 10^{-2}$	$8.13 \times 10^{-6}$	$1.02 \times 10^{-3}$

For purposes of comparison, reactions were carried out between these three solutions and iron, and these were exactly analogous with the reactions with nickel; *i.e.*, white ferrous chloride co-ordination compounds were formed with propyl alcohol and with acetic acid, but there was no reaction in nitrobenzene. Except in the case of liquids of similar structure, no connection was observed between dielectric constant of the liquid and the extent of ionisation of hydrogen chloride in it; *e.g.*, there was only a negligible ionisation of the hydrogen chloride in nitrobenzene ( $\epsilon_{20} = 36.1$ ), but a saturated solution in propyl alcohol ( $\epsilon_{20} = 12.3$ ) was strongly ionised. This does not agree with the Nernst-Thomson rule. Apparently the important factor affecting ionisation of the hydrogen chloride is the affinity of the solvent for the proton. Only when this affinity is sufficiently great to break down the covalent bond between the hydrogen and chlorine does ionisation take place.

It is of interest that no reaction took place between hydrogen chloride solutions in nitrobenzene and nickel or iron, although conductivity measurements indicate a slight ionisation of the solute. On the other hand, a vigorous reaction takes place between ethereal solutions of hydrogen chloride and both metals, without any ionisation of the hydrogen chloride.

Other nickel co-ordination compounds are being prepared, and it is hoped to advance reasons for apparent anomalies and to indicate the mechanism of the reactions in a later paper.

#### EXPERIMENTAL.

In all the experiments, the purest nickel powder obtainable was used. The details of purification of most liquids have already been given (*loc. cit.*). Pure *n*-propyl alcohol was dried with quicklime and distilled, head and tail fractions being neglected, and the product redistilled from calcium turnings; b. p. 96.6—97.4°/763 mm. Nitrobenzene was washed with dilute hydrochloric acid, then with aqueous potash, and finally with water. It was dried over fused calcium chloride and distilled, head and tail fractions being neglected; b. p. 209.8—210.5°/757 mm. Glacial acetic acid (m. p. 15.8°) was used without further purification.

The apparatus used was similar to that employed in the preparation of the corresponding chromium compounds (Chesterman, J., 1933, 796), with the following modifications. Fused ammonium chloride was used in a Kipp's apparatus instead of sodium chloride in a flask. Special reaction vessels of Pyrex glass were used, consisting of a 100 c.c. wash-bottle with a very wide ( $1\frac{1}{2}$ "') ground glass neck.

*Compounds with Methyl Alcohol.*—(1) Dry hydrogen chloride was passed into a suspension of nickel (*ca.* 3 g.) in 25 c.c. of methyl alcohol. After a short induction period the nickel began to dissolve, forming a green solution, and after nearly an hour a yellowish precipitate was deposited. When sufficient solid had collected, the liquid was decanted, and the compound together with any excess nickel was dried on a porous plate in a desiccator over calcium chloride. A portion of the dry powder was taken for analysis. It was dissolved in water, the unattached nickel collected in a sintered-glass crucible, washed, dried, and weighed, and nickel and chloride were estimated in aliquot parts of the main solution as dimethylglyoxime complex and silver chloride respectively (Found: Ni, 35.58; Cl, 43.20.  $\text{NiCl}_2 \cdot \text{CH}_4\text{O}$  requires Ni, 36.32; Cl, 43.80%).

(2) The dark green solution which was decanted from the reaction vessel in the previous experiment was filtered into a dish in a calcium chloride vacuum desiccator and left at atmospheric pressure. The tap in the vacuum desiccator was replaced by a calcium chloride tube so that there was no danger of pressure developing as the alcohol evaporated. Bright green crystals collected after some weeks, and were rapidly dried between previously dried filter papers (Found: Ni, 30.65; Cl, 39.00.  $\text{NiCl}_2 \cdot 2\text{CH}_4\text{O}$  requires Ni, 30.32; Cl, 36.63%). It was essential to analyse the *compound* immediately, for in the air it soon lost the extra alcohol molecule, forming the monomethyl alcoholate.

*Compound with Ethyl Alcohol.*—This 1:1-*compound* was prepared in a similar manner to the corresponding methyl alcohol compound, and was also a yellow powder soluble in water to a green solution (Found: Ni, 33.98; Cl, 41.95.  $\text{NiCl}_2 \cdot \text{C}_2\text{H}_6\text{O}$  requires Ni, 33.40; Cl, 40.39%).

The compound was prepared in a purer state by refluxing anhydrous nickelous chloride with absolute alcohol, an S-shaped calcium oxide tube at the top of the condenser preventing ingress of moisture. Nickelous chloride was added through the top of the condenser to the hot alcohol a little at a time until no more would dissolve. The hot solution was filtered and allowed to crystallise in a vacuum desiccator over calcium chloride. The yellowish-green crystals were dried on a plate over calcium chloride, losing their green tinge and becoming yellow (Found : Ni, 33.20; Cl, 41.18%).

*Compounds with n- and with iso-Propyl Alcohol.*—These compounds were prepared and analysed in a similar manner to that used for those of methyl alcohol. They formed greenish-yellow powders, but owing to the slowness of the reaction only a very small quantity of each could be obtained (Found, for Pr<sup>a</sup> compound; Ni, 35.7; Cl, 46.0; for Pr<sup>b</sup> compound; Ni, 35.3; Cl, 44.9. 2NiCl<sub>2</sub>.C<sub>3</sub>H<sub>8</sub>O requires Ni, 36.8; Cl, 44.4%). The colour of the solution in both cases was blue, indicating a change in structure, in agreement with their constitution as hemi-alcoholates. Both compounds crystallised far less readily than those with lower alcohols.

*Compounds with Acetic Acid.*—(1) The greyish-buff solid which was precipitated from the green solution in the reaction vessel was analysed after drying on a porous plate (Found : Ni, 36.21; Cl, 47.03. 2NiCl<sub>2</sub>.C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> requires Ni, 36.77; Cl, 44.43%).

(2) The green solution from the previous experiment was filtered into a crystallising dish and allowed to evaporate in a vacuum desiccator over calcium chloride and solid sodium hydroxide. A small quantity of very pale yellowish-white crystals was obtained (Found : Ni, 31.52; Cl, 36.88. NiCl<sub>2</sub>.C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> requires Ni, 30.96; Cl, 37.40%).

*Other Compounds.*—*With ether.* The greenish-yellow solution did not deposit crystals in the reaction vessel, but on evaporation in a desiccator, green crystals of the co-ordination compound were deposited (Found : Ni, 33.94; Cl, 42.66. NiCl<sub>2</sub>.C<sub>5</sub>H<sub>10</sub>O requires Ni, 35.23; Cl, 42.55%).

*With methyl acetate.* This compound was isolated in the form of a green powder by allowing the solution from the reaction vessel to evaporate in a vacuum desiccator over calcium chloride (Found : Ni, 35.23; Cl, 42.55. Ni : Cl : CH<sub>3</sub>.CO<sub>2</sub>CH<sub>3</sub> = 1 : 1.999 : 0.446). The loss of ester may be taken as indicating a weak link to the nickel atom.

*With ethyl acetate.* Only a trace of olive-green compound could be isolated, insufficient for analysis.

Most of the analyses indicate a rather high chloride content. This may be partly due to slight occlusion of hydrogen chloride by the crystals. Owing to the readiness with which nickelous chloride co-ordinates, it was thought unwise to wash the crystals with the usual organic solvents for hydrogen chloride. In addition, there is a possibility that a slight amount of direct combination with the hydrogen chloride takes place after some time.

In view of the similarity between nickel and iron compounds generally, it is of interest that, in nearly every case, ferrous chloride was able to co-ordinate with twice as many solvent molecules as nickelous chloride, under similar conditions; *e.g.*, corresponding compounds were :



Measurements of conductivity were carried out in the specially designed cell already described (Chesterman, J., 1935, 909), the hydrogen chloride being prepared as before and dried with anhydrous aluminium chloride. Instead of the sliding wire bridge, an accurate helicoid bridge calibrated by the makers (Messrs. Tinsley) was used.

The estimation of solubility in all these experiments was carried out gravimetrically, this being necessary in the case of acetic acid, because of the acid solution. About 4 c.c. of the saturated solution at atmospheric pressure and 25° were pipetted mechanically from the cell into a weighing bottle. This was closed, weighed, and then opened under water, the chloride being estimated by precipitation with silver nitrate solution in presence of dilute nitric acid.

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