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PREPARATION OF MIXED-LIGAND COMPLEXES OF NICKEL VIA THERMAL DECOMPOSITION

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If heated to around 270° in argon, [Ni(HSal)$_2$] (H_2Sal = salicylic acid) gives off gaseous H_2Sal and forms [NiSal], which reacts with monoprotic ligands HL (e.g. 8-hydroxyquinoline) to form mixed-ligand complexes [NiHSalL], or with diprotic ligands H_2L' (e.g. quadratic acid) to form dinuclear complexes [HSalNiL'NiHSal].

Preparations of complexes

Preparation of NiSal

Upon addition of an aqueous solution of a nickel salt to an aqueous solution of [NaHSal], the precipitate [Ni(HSal)$_2\cdot 3H_2O$] is formed. After drying in vacuum, thermogravimetric analysis (Fig. 1) reveals its conversion into [NiSal] at around 280°. Portions of around 6 g of [NiSal] were prepared by heating around 10 g of [Ni(HSal)$_2$] in a stream of argon for 1 h at 270°

Preparation of mononuclear complexes with two different ligands

[NiSal] is a very strong Brönsted base and therefore reacts with ligands containing an acidic proton, HL, to form mixed-ligand complexes [NiHSalL] according to reaction (1), illustrated in Fig. 2:

$$[\mathrm{NiSal}] + \mathrm{HL} = [\mathrm{NiHSalL}] \tag{1}$$

Complexes of this type have been prepared with the following L: acetylacetonate, anthranilate, dimethylglyoximate and oxyquinolate. An analogous reaction scheme has previously been used for the synthesis of some zinc complexes with two different ligands [1].

Preparation of binuclear complexes with two different ligands

Two moles of [NiSal] may react with one mole of the diprotic ligand H_2L. Since L' can function as a bridging ligand, binuclear complexes will be formed according

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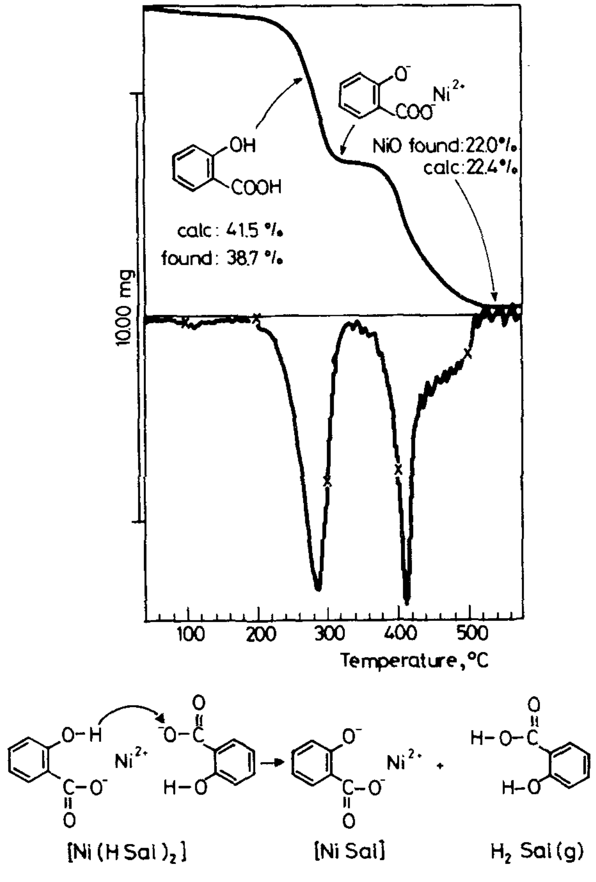

Fig. 1 Thermal decomposition of [$Ni(HSal)_2$]

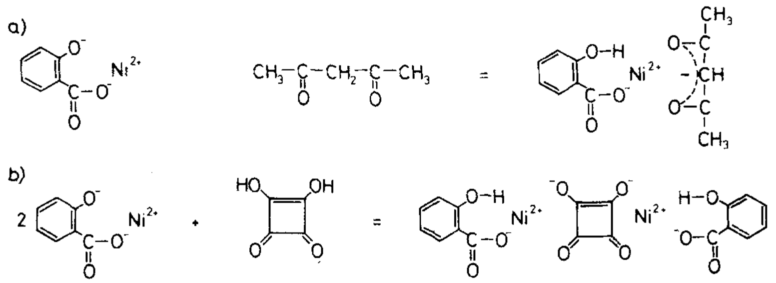

Fig. 2 Typical reactions of [NiSal] a) with a monoprotic acid forming a mononuclear complex, b) with a diprotic acid forming a binuclear complex

to reaction (2), illustrated in Fig. 2:

$$2\,[\mathrm{NiSal}] + \mathrm{H_2L'} = [\mathrm{HSalNiL'NiHSal}] \qquad (2)$$

Binuclear complexes with bridging ligands derived from the following acids H_2L' were prepared: 3,4-dihydroxy-3-cyclobutene-1,2-dione (= quadratic acid), biimidazole 2 and oxalic acid. In a similar fashion, [HSalZn · chloranilate · ZnHSal] has been prepared [3].

Experimental

In general, reactions (1) or (2) take place if a suspension of [NiSal] is refluxed for several hours in toluene containing a stoichiometric amount of dissolved or suspended acidic ligand HL or H_2L'. A second synthetic method consists in pressing a tablet of intimately mixed powders of [NiSal] and HL or H_2L', and annealing it in argon for around one day in a closed tube at the highest possible temperature, where no HL or H_2L' is lost by volatilization.

Characterization of the products

It is very difficult to characterize unambiguously these complexes with two different ligands; this is a jigsaw puzzle which may never be complete, but the missing pieces will hopefully not change the picture fundamentally.

A first indication of the formation of the desired complex is its TG curve, which will be different from the one of a mixture of the reactants and also different from the products of the most probable, yet undesired side-reaction (3):

$$2\,[\mathrm{NiSal}] + 2\,\mathrm{HL} = [\mathrm{Ni(HSal)_2}] + \mathrm{NiL_2} \qquad (3)$$

As an example, one may consider Figs 1, 3 and 4, where the thermogravimetric curves of $[\mathrm{Ni(HSal)_2}]$, [Ni quadratate] and [HSalNi · quadratate · NiHSal] indicate formation of the latter.

If the complexes are prepared by reacting two solids, either as a toluene suspension or as a pressed tablet, the stoichiometry of the product is not very meaningful information, However, the X-ray powder diagrams of the reactants and the products show whether the mixture has reacted or not. Further, the powder diagrams of the products of the undesired reaction (3) are easily measured, and therefore the occurrence of reaction (3) can be detected [1]. Instead of the X-ray powder diagrams, or supplementary to them, the IR spectra of the reactants and products may be compared.

Unfortunately, the UV–VIS spectra of the powder samples are poorly resolved

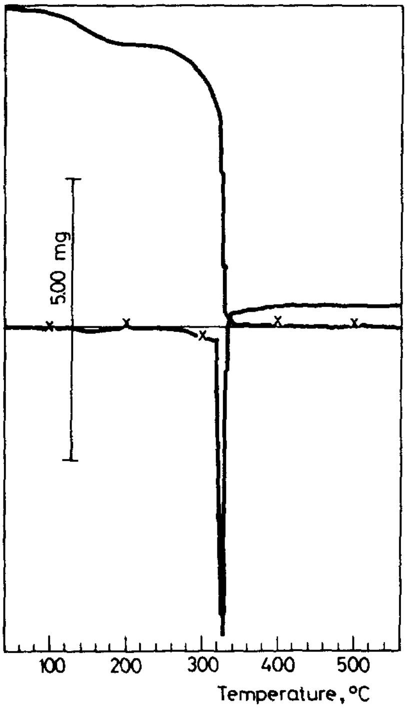

Fig. 3 TG and DTG curves of [Ni quadratate]

and, in spite of noticeable differences (e.g. in the case of [NiHSal·dimethylglyoximate] and [Ni(dimethylglyoximate)$_2$]), they cannot be interpreted in terms of the ligand field shifts of the different coordinating atoms N and O, and they are therefore not very valuable for characterization of the complexes.

In some cases, valuable information can be gained from the solubilities of the reactants or of the products. For instance, if insoluble [NiSal] is refluxed with a toluene solution of 8-hydroxyquinoline, the poorly-soluble mixed-ligand complex [NiHSal·oxyquinolate] is formed by taking the hydroxyquinoline out of the solution. This is indicated by the weight increase of the precipitate, and is proven by its elemental analysis: $NiC_{16}N_{11}NO_4$ (calculated values in parentheses) C: 56.31% (56.53), H: 3.35% (3.26), N: 4.33% (4.12), NiO: 21.22% (21.97).

On the other hand, acetylacetone and [NiSal] react by forming the appreciably toluene-soluble mixed complex [Ni-HSal·acac]. As [NiSal] and [Ni(HSal)$_2$] are insoluble in toluene, the mere fact that appreciable quantities of a salicylate-containing nickel complex are dissolved in toluene is a strong indication of the

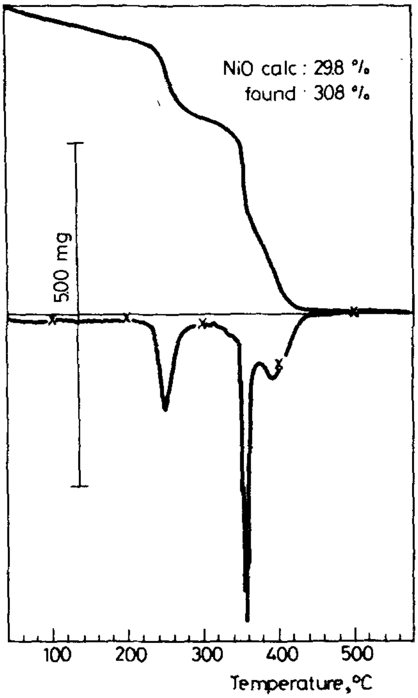

Fig. 4 TG and DTG curves of [HSalNi quadratate NiHSal]

formation of a mixed-ligand complex. The result is supported by elemental and thermogravimetric analyses.

No attempt has been made to investigate the cis-trans isomerism of these complexes.

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Zusammenfassung — Die Komplexverbindung [Ni(HSal)$_2$] spaltet beim Erhitzen auf 270 °C in Argon Salicylsäure ab und liefert [NiSal], das mit Monoproton-Liganden HL (z. B. 8-Hydroxychinolin) zu Gemischtliganden-Komplexen [NiHSalL], mit Zweiprotonen-Liganden H$_2$L′ (z. B. Quadratsäure) dagegen Zweikernkomplexe [HSalNiL′NiHSal] bildet.

Резюме — При нагревании салицилата никеля [Ni(HSal)$_2$] в атмосфере аргона до температуры 270°, выделяется газообразная салициловая кислота и образуется комплекс [NiSal], которые реагируют с монопротонированными лигандами HL (напр., 8-оксихинолином) с образованием комплексов со смешанным лигандом [NiHSalL] или с дипротонированными лигандами H$_2$L′ с образованием двуядерных комплексов [HSalNiL′NiHSal].