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SYNTHESIS AND THERMAL STUDY OF SOME ADDUCTS OF MORPHOLINE WITH NICKEL(II) NITRITE, SULPHATE AND PERCHLORATE

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The preparations of the nickel-morpholine *(Morph)* complexes $Ni(NO_2)_2 \cdot 3Morph$ and $Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$ are described. The thermal treatment of this perchlorate and of $NiSO_4 \cdot 2Morph$ led to the isolation of $Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$ and $NiSO_4 \cdot Morph$. The magnetic moments, diffuse reflectance spectra and infrared spectra of these compounds are all compatible with a pseudo-octahedral environment around the nickel atom.

The complexes of morpholine, a six-membered heterocyclic ligand containing two donor sites (O and N atoms), with nickel(II) have been the subject of a number of synthetic and characterization studies [1–7]. In these complexes, morpholine may act either as a monodentate or as a bridging bidentate ligand, the former kind of behaviour being the usual one. The thermal treatment of nickel complexes containing morpholine has shown to be a useful method for the preparation of intermediates which cannot be isolated directly through the reaction of nickel salts with morpholine [6, 7].

As a continuation of our preparative and thermal studies on nickel(II)-morpholine compounds, the behaviour of morpholine towards the title nickel salts has been investigated. $NiSO_4 \cdot 2Morph$ was previously prepared by Ahuja [1], whereas the preparations of $Ni(NO_2)_2 \cdot 3Morph$ and $Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$ are described here for the first time. $NiSO_4 \cdot Morph$ and $Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$ have been isolated as reaction intermediates on the thermal treatment of their respective precursors.

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Experimental

Reagent and solvents

Morpholine and 2,2-dimethoxypropane were purchased from May and Baker Ltd. and Fluka, respectively, and used as received. The nickel salts were commercial products. $NiSO_4 \cdot 2Morph$ was prepared according to [1]. Diethyl ether was distilled over sodium in the presence of benzophenone and was kept over sodium wire. Methanol was dried with calcium oxide for 1 day, then distilled in the presence of magnesium powder, and finally kept over molecular sieves of 3 Å.

Methods

C, H and N analyses were carried out in a Perkin–Elmer 240C microanalyser and nickel was determined by edtametry [8]. The infrared spectra of the studied compounds in Nujol mulls or KBr pellets were recorded with a Perkin–Elmer 457 spectrophotometer. The diffuse reflectance spectra were recorded on a Beckman DK–2A spectrophotometer, with Nujol mulls smeared on filter paper between two glass plates. TG curves were obtained under dynamic atmospheres of air and nitrogen in a Netzsch STA–429 thermobalance; Al_2O_3 was used as reference material. Magnetic susceptibilities were measured by the Faraday method, using a Cahn RG 2102 electrobalance and a Systron Conner 6001 electromagnet with $Co[Hg(SCN)_4]$ [9].

Preparation of the complexes

$Ni(NO_2)_2 \cdot 3Morph$.-2,2-Dimethoyypropane (12 ml) was added to 20 ml of a 0.5 *M* solution of nickel nitrite in methanol, prepared as described in [10]. The solution was refluxed and stirred for 5 h, and morpholine (12 ml) was then added under N_2 atmosphere. Addition of diethyl ether caused the formation of a green precipitate; which was filtered off. The resulting solution was concentrated under vacuum and diethyl ether was added. After standing for 24 h, blue-green crystals were obtained, which were filtered off and washed with diethyl ether under N_2. They were dried under vacuum. Yield 19%.

$Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$.—A suspension of $Ni(ClO_4)_2 \cdot 6H_2O$ (1 g) in 2,2-dimethoxypropane (10 ml) was refluxed for 6 h. After cooling, morpholine (7 ml) was added dropwise. The sticky green product which resulted was transformed into a powder by stirring. The solid was separated by filtration, washed with diethyl ether and dried under vacuum. The green-yellow solid was kept in a P_2O_5-desiccator because it was very hygroscopic. Yield 89%.

Results

Thermal behaviour

TG and DTA curves of $Ni(NO_2)_2 \cdot 3Morph$, $NiSO_4 \cdot 2Morph$ and $Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$ are shown in Figs 1–3. They were recorded at a heating rate of 5 deg min^{-1}.

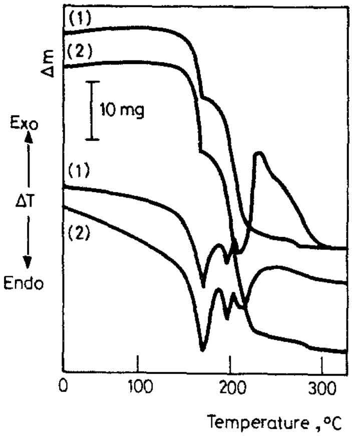

Fig. 1 Simultaneous TG and DTA curves of thermal decomposition of $Ni(NO_2)_2 \cdot 3Morph$. (1) air, 48.6 mg; (2) N_2, 64.5 mg

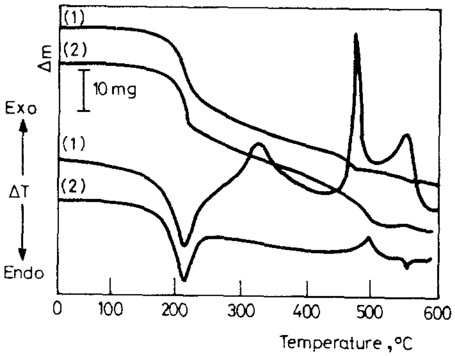

Fig. 2 Simultaneous TG and DTA curves of thermal decomposition of $NiSO_4 \cdot 2Morph$. (1) air, 58.4 mg; (2) N_2, 55.8 mg

It follows from an analysis of the TG and DTA curves that the behaviour of $Ni(NO_2)_2 \cdot 3Morph$ is similar in nitrogen and air, but in air an additional exothermic peak is observed at the end of the thermal decomposition. On heating, morpholine is released in two distinctly marked steps: at 135–175° (weight loss 25.3%) and 175–240° (weight loss 50%). They are accompanied by three

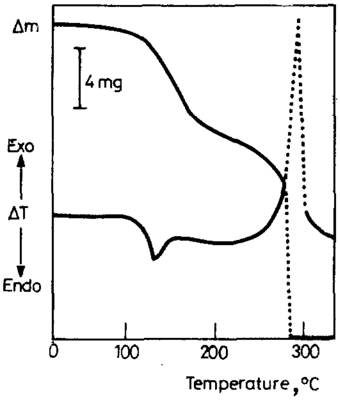

Fig. 3 Simultaneous TG and DTA curves of thermal decomposition of $Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$ in N_2, 70.5 mg

endothermic DTA peaks, at 170, 200 and 210°, respectively. The first peak is attributed to the release of morpholine, and the others to the loss of the remaining morpholine and the decomposition of nitrite, these two processes being indistinguishable in the TG trace. Finally, after a slight weight loss, a plateau is reached (at 300° in air, and at 320° in nitrogen) with the formation of NiO. In air, the exothermic peak observed at 228° (DTA) is attributed to the combustion of morpholine. The weight loss in the first step is larger than the theoretical value for one morpholine mol (21.1%) and attempts to isolate a $Ni(NO_2)_2 \cdot 2Morph$ intermediate were unsuccessful.

In nitrogen, $NiSO_4 \cdot 2Morph$ loses one morpholine molecule between 112 and 222°, to give $NiSO_4 \cdot Morph$. The process is endothermic, with a DTA peak at 212°. $NiSO_4 \cdot Morph$ is an isolable solid which decomposes between 222 and 570°, but the experimental weight loss is larger than that expected for one morpholine molecule, because the release of morpholine and the decomposition of $NiSO_4$ to NiO overlap. In fact, at 575° the residue is identified as NiO (23.3% against the theoretical value of 22.7%). The exothermic DTA peak at 495° is attributed to a redox reaction between the sulphate group and organic material from the decomposition of morpholine, and the endothermic peak at 565° to the decomposition of the remaining nickel sulphate to nickel oxide. In air, the behaviour is similar to that observed in nitrogen for the first decomposition stage, but it is otherwise different. Thus, the final product is not nickel oxide, but a mixture of nickel oxide and nickel sulphate (weight loss 36.7% against the theoretical value of 50.8% for the formation of NiO). Three exothermic peaks are observed in the DTA curve, at 322, 475 and 560°, respectively, the first being attributed to the combustion of morpholine and the others to the combustion of organic residue.

Because of the explosive nature of its thermal decomposition, $Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$ was studied only under nitrogen atmosphere, diluted in alumina. Two morpholine molecules are released between 98 and 175°, and $Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$ can be isolated as a reaction intermediate by heating at 110° until constant weight. The maximum of the endothermic DTA effect lies at 135°. The intermediate species decomposes slowly between 175 and 270°, but at the latter temperature the decomposition becomes explosive, the substance being ejected from the crucible. The weight loss in the first stage (27.6%) fits quite well the calculated value (27.1%) for the elimination of two morpholine molecules.

Structural study

The analytical data on the new nickel complexes are listed in Table 1. The magnetic moments and electronic spectra of the compounds (Table 2) are all compatible with the assignment of a pseudo-octahedral environment around the nickel atom.

Table 1 Colours and analytical data on the new nickel compounds

Compound	Colour	Analysis (%)*			
		C	H	N	Ni
$Ni(NO_2)_2 \cdot 3Morph$	Green	34.8 (35.0)	6.8 (6.6)	16.7 (17.0)	14.5 (14.3)
$NiSO_4 \cdot Morph$	Pale yellow	19.7 (19.9)	3.9 (3.7)	5.4 (5.8)	—
$Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$	Yellow-green	29.8 (29.9)	6.1 (6.2)	8.8 (7.7)	9.2 (9.1)
$Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$	Yellow-green	20.6 (20.5)	4.5 (4.7)	6.2 (6.0)	—

* Calculated values in parentheses.

Table 2 Magnetic moments and diffuse reflectance spectra

Compound	(BM)*	Electronic bands, cm^{-1}
$Ni(NO_2)_2 \cdot 3Morph$	3.42	9,805; 16,155
$NiSO_4 \cdot Morph$	3.13	7,325sh; 8,370; 13,985
$Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$	3.43	8,930; 15,200
$Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$	3.25	7,355sh; 8,620; 15,270

* At room temperature

Table 3 Infrared data of $\bar{\nu}$(N—H) of coordinated morpholine

Compound	$\bar{\nu}$(N—H)*, cm^{-1}
$Ni(NO_2)_2 \cdot 3Morph$	3220s, 3180s
$NiSO_4 \cdot Morph$	—
$Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$	3170
$Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$	3205s, 3149s

* At *ca.* 3300 cm^{-1} in uncomplexed morpholine [12]

The electronic spectrum of $Ni(NO_2)_2 \cdot 3Morph$ shows two bands, at 9,805 and 16,155 cm^{-1}, which may be assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, respectively. The ν_2/ν_1 ratio, 1.65, is in the range expected for fairly octahedral complexes of nickel(II) [11]. The infrared spectrum reveals that morpholine acts as a monodentate N-donor ligand, since ν(N—H) appears at a lower wavenumber than in uncomplexed morpholine (Table 3) [12], and no splitting is observed for the stretching modes corresponding to the fundamentals, for which the greatest contribution is made by the C—O—C stretch, *i.e.*, ν_{14} and ν_{32}, at *ca.* 1030 and 1200 cm^{-1}, respectively [12]. Three absorptions, observed at 1385, 1220 and 830 cm^{-1}, may be attributed to the ν_{as}, ν_s and δ vibrations of the NO_2 group as monodentate O-donor ligand [13]; two additional bands, at 1270 and 860 cm^{-1}, are consistent with the presence of NO_2 as bidentate ligand [13]. Moreover, the absence of absorption at *ca.* 620 cm^{-1} for the wagging mode of NO_2 rules out the possibility of interaction of the NO_2 group via the nitrogen atom [13]. The compound is very soluble in acetone and methanol, and the molar conductance of an acetone solution ($\sim$0.007 *M*) is $\Lambda_M = 9.8$ cm^2 ohm^{-1} mol^{-1}, corresponding to a non-electrolyte [14]. The above data suggest a pseudo-octahedral structure containing monodentate N-donor morpholine, monodentate nitrite, and bidentate nitrite. It should be mentioned at this point that a similar structural situation was found in $Ni(NO_3)_2 \cdot 3Morph$ [4].

Although the data in Table 2 also suggest a pseudo-octahedral structure for all the other compounds, it should be noted that the shoulders of the first band in the electronic spectra of $NiSO_4 \cdot Morph$ and $Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$ are indicative of an appreciable distortion of the O_h symmetry.

The infrared spectrum of $NiSO_4 \cdot Morph$ displays a broad absorption centred at 1100 cm^{-1}, with three peaks at 1150, 1100 and 1030 cm^{-1}, although the resolution is not good enough. The splitting can be attributed to the presence of a bridging sulphate group [1]. If the $NiSO_4 \cdot Morph$ stoichiometry is taken into account, the hexacoordination of the metal atom can be achieved by sharing both the sulphate group and the morpholine. Unfortunately, no structural information about morpholine can be deduced from the infrared spectrum, because the broad absorption from the sulphate group masks the 1100–1000 cm^{-1} region where ν(C—N—C) and ν(C—O—C) should be found.

The infrared spectrum of $Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$ shows two peaks, at 3648 and 3620 cm^{-1}, assignable to ν_{asym} and ν_{sym} of coordinated water, along with a shoulder at 1630 cm^{-1} (δHOH) on a band at 1570 cm^{-1} (NH def.). A broad, strong absorption at 1100 cm^{-1} indicates that the perchlorate group is present as the free ion (T_d symmetry), and the compound should be formulated as $[Ni(Morph)_4(H_2O)_2](ClO_4)_2$. The infrared spectrum of $Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$ also displays the bands of coordinated water at 3648, 3620 and 1620 cm^{-1}, but again the band at 1100 cm^{-1} from the ClO_4 group masks the region which should provide structural information about morpholine.

The difference in behaviour observed for the sulphate and perchlorate compounds is clearly a consequence of the different abilities of the two anions to take part in coordination. Thus, in $NiSO_4 \cdot 2Morph$ there is coordinated sulphate [1], whereas in $Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$ two H_2O molecules occupy the two coordination sites not filled by the less strongly donating perchlorate. Nevertheless, when the infrared spectra of the two perchlorate compounds described here were recorded in KBr pellets, a drastic change was observed, the major difference being the disappearance of the absorptions from coordinated water and the splitting of the 1100 cm^{-1} band from the perchlorate group.

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Zusammenfassung — Die Darstellung der Nickel-Morpholin(Morph)-Komplexe $Ni(NO_2)_2 \cdot 3Morph$ und $Ni(ClO_4)_2 \cdot 4Morph \cdot 2H_2O$ wird beschrieben. Die thermische Behandlung dieses Perchlorates und von $NiSO_4 \cdot 2Morph$ ergibt $Ni(ClO_4)_2 \cdot 2Morph \cdot 2H_2O$ und $NiSO_4 \cdot Morph$. Magnetisches Moment sowie diffuse Reflektionsspektren und Infrarotspektren dieser Verbindungen sind kompatibel mit einer pseudooktaedrischen Koordination des Nickelatoms.

Резюме — Описано получение аддуктов нитрита, сульфата и перхлората никеля с морфолином (Морф) следующего состава: $Ni(NO_2)_2 \cdot 3$Морф, $NiSO_4 \cdot 2$Морф и $Ni(ClO_4)_2 \cdot 4$Морф$\cdot 2H_2O$. Термическая обработка двух последних соединений привела к выделению соединений $NiSO_4 \cdot$ Морф и $Ni(ClO_4)_2 \cdot 2$Морф$\cdot 2H_2O$. Магнитные моменты, спектры диффузного отражения и ИК спектры показали, что эти соединения обладают псевдооктаэдрической структурой.