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TETRACYANONICKELATES CONTAINING ETHYLENEDIAMINE LIGANDS ISOLATED AT DIFFERENT pH VALUES AND THEIR THERMAL STABILITIES

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ABSTRACT

This study of tetracyanonickelates having the general formula $Ni(en)_mNi(CN)_4 \cdot nH_2O$ ($m = 1$, 2 or 3 and $n > 0$) was performed in order to determine the influence of the pH value of the solution during synthesis on the composition and thermal stability of these compounds. It was revealed during the synthesis of these compounds that the pH value of the medium affects both the number of ethylenediamine ligands and the amount of water present.

INTRODUCTION

The investigation into the composition and properties of tetracyanonickelates of the general formula $Ni(en)_mNi(CN)_4 \cdot nH_2O$ as a function of pH during their synthesis is a continuation of the preceding papers [1,2] dealing with the clathrate compounds of general formula $Ni(NH_3)_mNi(CN)_4 \cdot nH_2O$.

It appears that, in synthesizing the model compound of the host component of inclusion compounds of the clathrate type, having the general formula $Ni(NH_3)_2Ni(CN)_4 \cdot nG$, where G is the guest component, the host component containing a certain amount of water enclosed in the interlayer space is obtained from aqueous solutions. Thus, it is a clathrate compound containing water as a guest component.

Rayner and Powell [3] were the first to determine the layer structure of the clathrate compound $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$. The structural data of the compound $Ni(B)_2Ni(CN)_4 \cdot nG$ ($B = NH_3, H_2O$ and $G = H_2O, C_6H_6$) were known from other publications [4-6].

The amount of water enclosed within the layers is dependent on the pH of the medium during isolation of the compound from solution [1,2]. A decrease in pH towards more acid values results in separation of the layers of the host lattice, and, thus, in formation of a larger space for the entrapment of water molecules. The number of ammine ligands does not vary within the pH range 5-8.

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It has been found by combining DSC and GC methods with infrared spectroscopy [1] that the compound $Ni(NH_3)_2Ni(CN)_4 \cdot nH_2O$ exhibits sorptive properties. The study of the sorptive properties of this compound with respect to different organic mixtures was the topic of other papers from our department [7,8]. The sorptive properties were significantly improved by additional treatment of this compound with different auxiliary solvents [8]. 1,4-Dioxane had the most significant effect [7].

The purpose of our investigations of the synthesis of tetracyanonickelates containing ethylenediamine ligands at varying pH values of the medium was to obtain products containing different amounts of water and ethylenediamine ligands and exhibiting sorptive or other interesting properties.

EXPERIMENTAL

Syntheses

The syntheses of the compounds of general composition $Ni(en)_mNi(CN)_4 \cdot nH_2O$ were investigated at varying pH values of the medium during their isolation from solution in the solid state. The experiences obtained from our earlier investigations were applied to these experiments [1,2].

All starting compounds were analytical grade chemicals. $NiSO_4 \cdot 7H_2O$, or, if necessary, another nickel(II) salt such as $NiCl_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 9H_2O$, was used as a source of nickel(II). The pH measurements of the solutions were carried out using a Radelkis (Budapest) pH-meter, type OP-208, equipped with a glass and calomel electrode.

By mixing solutions of KCN and $NiSO_4$, a precipitate of $NiNi(CN)_4 \cdot nH_2O$ was obtained. (The solution of KCN was prepared by dissolving 1.5 g of KCN in 25 cm^3 of H_2O, and the solution of $NiSO_4$ was obtained by dissolving 3 g of $NiSO_4 \cdot 7H_2O$ in 25 cm^3 of H_2O). The precipitate was dissolved in a 1 M solution of ethylenediamine (about 40 cm^3). Thus we obtained a violet solution of pH 12 from which violet-pink crystals having the composition $Ni(en)_3Ni(CN)_4 \cdot H_2O$ separated after some time. This precipitate may be obtained immediately by using more concentrated solutions.

In order to bring down the pH value of the solution, to remove some of the ethylenediamine ligands, and to obtain the products in the solid state, acetic acid (60%) was added to the solution of $[Ni(en)_m][Ni(CN)_4]$ ($m > 3$) (this solution may also be diluted with a small amount of water to prevent crystal formation) with intensive stirring and cooling with ice. By reducing the pH of the solution from 12 stepwise to 8, 7, 6, 5 and 4, and gradually isolating the product at each of these pH values, pink precipitates were obtained. These precipitates were washed with a small amount of cold water and dried in a desiccator over silica gel.

The pH values of the medium used for the synthesis of the compounds of the above composition were chosen according to the results of continuous potentiometric titration of the solution of $[Ni(en)_m][Ni(CN)_4]$ with acetic acid.

Analyses

The prepared compounds were analysed using a Hewlett–Packard CHN-model 185. Nickel(II) was determined complexometrically.

The water present in the prepared compounds was estimated by gas chromatography. A chromatograph SCH-7801 (Prague, Satalice, Czechoslovakia), a TCD detector and hydrogen carrier gas were used. The measurements were performed with a column (length 2 m), packed with Porapak Q, at 130 °C. The working procedure was as follows. The solid compound (200 mg) in a sealed glass ampoule (2.5–3 cm^3) was heated to the temperature necessary to release the water, according to results of thermal analysis. This process resulted in the ampoule possessing a closed capillary. After cutting the sealed end of the capillary, a sample of the water vapour liberated from the compound was collected with a syringe (1 μl) and introduced into the chromatograph.

The composition of all compounds and intermediates identified by thermal analysis was confirmed by infrared spectra taken on a Specord IR 75 (Carl Zeiss, Jena) using the KBr or nujol technique.

Thermal decomposition

All synthesised compounds were subjected to thermal analysis (TG, DTG and DTA methods) in an air atmosphere up to 600 °C. A MOM OD 102 derivatograph (Paulik–Paulik–Erdey, Budapest) was used for this purpose under the following conditions: weighed amount 100 mg; sensitivities: TG 100 mg, DTA $\frac{1}{5}$, DTG $\frac{1}{5}$; heating rate 6 °C min^{-1}; reference material Al_2O_3; ceramic crucible.

RESULTS AND DISCUSSION

The investigations of the compounds of the $Ni(en)_mNi(CN)_4 \cdot nH_2O$ type have shown that the composition and properties of these substances are affected by the pH value of the medium during synthesis. However, other experimental conditions may not be neglected.

The isolation of the products at pH 12, 8, 7, 6, 5 and 4 gave pink precipitates in which the number of ethylenediamine ligands and the water content was dependent on the pH value of the solution. The number of ethylenediamine ligands decreased with decreasing pH.

TABLE 1

Results of CHN analyses and nickel determination in compounds of the type $Ni(en)_mNi(CN)_4 \cdot nH_2O$

$Ni(en)_mNi(CN)_4 \cdot nH_2O$				C (%)	H (%)	N (%)	Ni (%)
Ph	m	n					
12	3	1	theor.	28.62	6.24	33.36	27.97
			exp.	28.67	6.42	33.09	28.17
8	2	3	theor.	24.28	5.60	28.32	29.67
			exp.	24.40	5.71	28.35	29.34
7	2	3	theor.	24.28	5.60	28.32	29.67
			exp.	24.43	5.64	28.32	30.12
6	1	1.8	theor.	22.95	3.72	26.76	37.39
			exp.	23.08	3.60	26.30	37.56
5	1	2	theor.	22.69	3.81	26.46	36.97
			exp.	22.65	3.56	26.12	36.78
4	1	2.7	theor.	21.81	4.09	25.45	35.56
			exp.	21.50	4.00	24.92	35.99

The compound isolated from the solution at pH 12 contained three ethylenediamine ligands and one mole of water. The results of the analyses (Table 1) show that the compounds isolated at pH 8 and 7 contained two ethylenediamine ligands, yet the amount of water increased when compared with the compound isolated at pH 12. Only one ethylenediamine ligand was present in the compounds isolated at pH 6, 5 and 4, and the amount of water slightly increased with decreasing pH.

According to the results of the analyses, the compounds of general composition $Ni(en)_mNi(CN)_4 \cdot nH_2O$ isolated in the investigated pH region may be divided into three classes: those with three ethylenediamine ligands (pH 12), those with two ethylenediamine ligands (pH 8 and 7), and those with one ethylenediamine ligand (pH 6, 5 and 4).

The infrared spectra of the compounds isolated from solutions at pH 12, 7 and 4 are shown in Fig. 1. The spectra of compounds isolated at pH 6 and 5 are very similar to the spectrum of that isolated at pH 4. The differences in water content manifest themselves as differences in the intensity of H_2O absorption bands.

There are two bands of strong intensity corresponding to $\nu(H_2O)$ which appear in the regions of 3650 and 3580 cm^{-1} for the compounds obtained at pH 6, 5 and 4. Provided the samples have been heated to 200 °C, the intensity of these bands only decreases slightly. After heating the sample to 350 °C, these bands vanish. The fact that they do not completely disappear on heating to 200 °C may be due to partial sorption of air humidity during measurement of infrared spectra by the KBr technique.

The absorption bands corresponding to the stretching vibrations of the NH_2 groups of ethylenediamine are visible in the region from 3360 to 3160

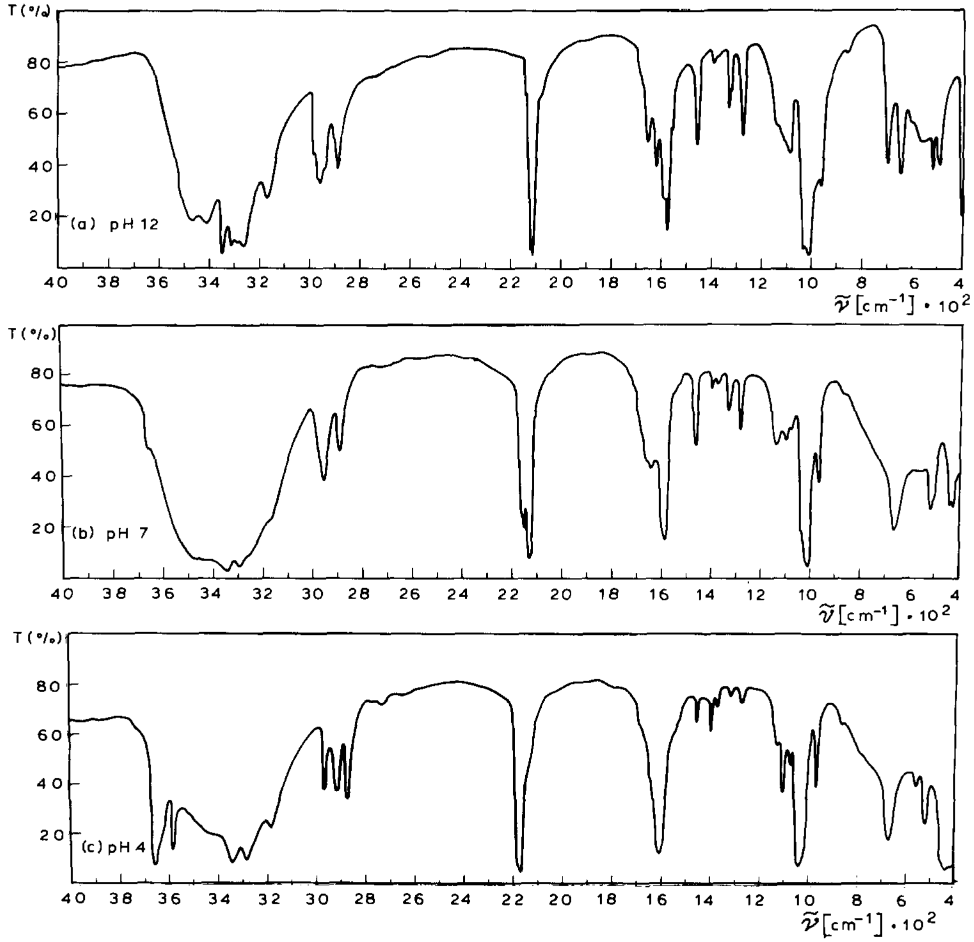

Fig. 1. Infrared spectra of (a) $Ni(en)_3Ni(CN)_4 \cdot H_2O$, pH 12; (b) $Ni(en)_2Ni(CN)_4 \cdot 3H_2O$, pH 7; (c) $Ni(en)Ni(CN)_4 \cdot 2.7H_2O$, pH 4.

cm^{-1}. The infrared spectrum of free ethylenediamine [9] shows the $\nu(NH_2)$ bands at 3335, 3246 and 3171 cm^{-1}.

The compounds prepared at pH 8 and 7 exhibit a rather broad absorption band in the region between 3655 and 3160 cm^{-1} where the bands assigned to the stretching vibrations $\nu(H_2O)$ and $\nu(NH_2)$ overlap. According to the literature [10], the broad absorption band in this region corresponds to the existence of an intramolecular hydrogen bond involving the OH groups of water and the NH_2 groups of the host lattice.

As for the compounds prepared at pH 6, 5 and 4, there are three distinct bands of medium intensity in the region between 2950 and 2850 cm^{-1}. They can be assigned to $\nu(CH_2)$ of ethylenediamine. On the other hand, the compounds prepared at pH 12, 8 and 7 exhibit only two bands in this region. If the compounds isolated at pH 12, 8 and 7 are heated to 260–270 ° C, these bands split to give three bands in this region like the compounds containing a single ethylenediamine ligand.

All these cyanocomplexes give rise to an intensive absorption band $\nu(C\equiv N)$ in the region 2160–2115 cm^{-1}.

The bands assigned to $\delta(H_2O)$ and $\delta(NH_2)$ appear in the region 1650–1580 cm^{-1}. Free ethylenediamine [9] exhibits the bands of bending vibrations of the NH_2 groups at 1608 and 1597 cm^{-1}.

If any sample obtained at the above-mentioned pH values is heated to 350–360 ° C, the bands corresponding to ethylenediamine disappear which indicates that it has escaped from the sample.

Gas chromatography gave qualitative evidence of the existence of water released from the prepared compounds on the basis of a comparison of the retention times of the released water and the water coming from a sample of pure H_2O.

The results of the thermal analysis have shown that the compounds isolated in the investigated pH range differed in the course of thermal decomposition which depended on the content of the ethylenediamine ligands.

The compound isolated at pH 12 which has the composition $Ni(en)_3Ni(CN)_4 \cdot H_2O$ is stable up to 60 ° C. Thermal decomposition (Fig. 2) begins with the loss of a mole of water in an endothermic process. A mole of ethylenediamine escapes in the second endothermic process manifesting itself by a maximum on the DTA curve at 225 ° C. The second mole of ethylenediamine is released in the course of an exothermic process taking place in the temperature interval 265–320 ° C. The third mole of ethylenediamine is split off in a further exothermic process above 320 ° C where the simultaneous decomposition of the cyanide groups begins.

The thermal decomposition of the sample isolated at pH 8 (Fig. 3) is the same as that of the sample isolated at pH 7, the composition of which was $Ni(en)_2Ni(CN)_4 \cdot 3H_2O$. The thermal decomposition starts by release of the three water molecules. The first mole of ethylenediamine is lost during an exothermic process in the temperature interval 240–320 ° C. The second mole of ethylenediamine is released in a rather exothermic process which also involves the decomposition of cyanides, as is apparent from the IR spectra. The final product of thermal decomposition at 430 ° C is nickel which is subsequently oxidised in air atmosphere to NiO.

The compounds isolated at pH 6, 5 and 4 (Fig. 4) correspond to the general composition $Ni(en)Ni(CN)_4 \cdot nH_2O$ i.e. these compounds contain only one ethylenediamine ligand. The water contents for pH 6, 5 and 4 are $n = 1.8$, $n = 2$ and $n = 2.7$, respectively. The first substance to be released during the thermal decomposition is water, once again. For the sample isolated at pH 4 (Fig. 4(b)), water escapes in two steps, as occurs in compounds containing ammine ligands [5] ($B = NH_3$, provided $n > 2$). The release of ethylenediamine proceeds in a manner analogous with the preced-

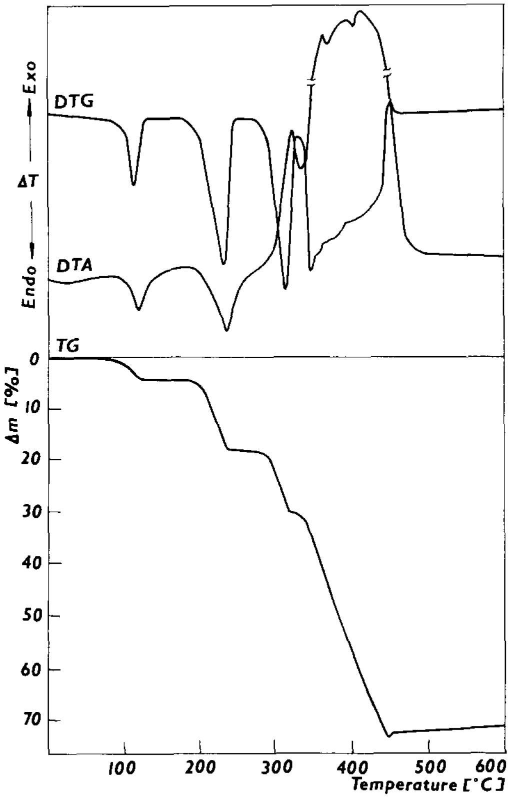

Fig. 2. TG, DTG and DTA curves of $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (pH 12).

TABLE 2

Percentage of H_2O and $C_2H_8N_2$ in compounds of the type $Ni(en)_mNi(CN)_4 \cdot nH_2O$

pH	Compound		$C_2H_8N_2$ (%)			H_2O (%)
			en	en	en + $(CN)_2$	theor./exp.
12	$Ni(en)_3Ni(CN)_4 \cdot H_2O$	theor.	14.27	14.27	14.27 + 24.79	4.29
		exp.	14.5	13.5	39.0	4.5
8	$Ni(en)_2Ni(CN)_4 \cdot 3H_2O$	theor.	–	15.19	15.19 + 26.30	13.66
		exp.		15.0	42.0	13.5
7	$Ni(en)_2Ni(CN)_4 \cdot 3H_2O$	theor.	–	15.19	15.19 + 26.30	13.66
		exp.		14.8	42	13.5
6	$Ni(en)Ni(CN)_4 \cdot 1.8H_2O$	theor.	–	–	19.14 + 33.14	10.33
		exp.			52	10.5
5	$Ni(en)Ni(CN)_4 \cdot 2H_2O$	theor.	–	–	18.92 + 32.77	11.32
		exp.			52	11.5
4	$Ni(en)Ni(CN)_4 \cdot 2.7H_2O$	theor.	–	–	18.20 + 31.51	13.76
		exp.			48.5	14.0

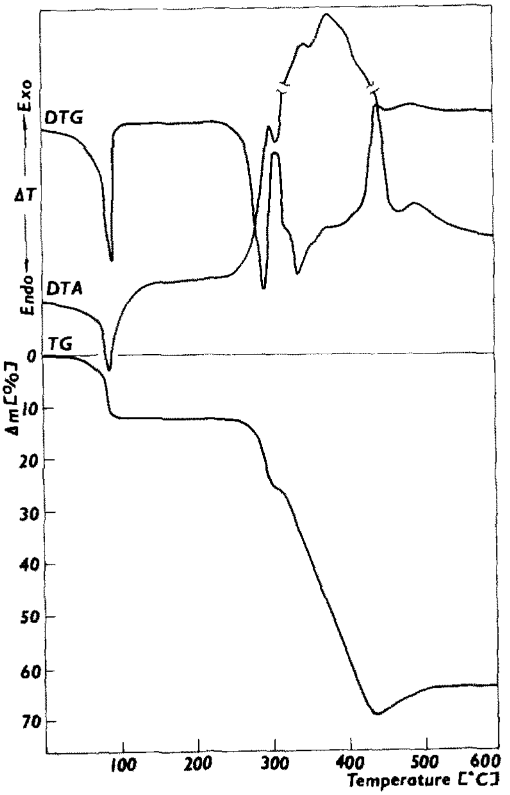

Fig. 3. TG, DTG and DTA curves of $Ni(en)_2Ni(CN)_4 \cdot 3H_2O$ (pH 8, 7).

ing compounds, in a rather exothermic process starting at 280 °C. The liberation of the last portions of ethylenediamine is accompanied by the decomposition of the cyanides. The final product of thermal decomposition is NiO.

The percentages of water and ethylenediamine in the investigated compounds determined by thermal analysis are given in Table 2.

The distribution of the compounds prepared in the above-mentioned pH range into three classes which differ in properties, composition and structure was further confirmed by the first results obtained by measuring the reflectance spectra in the ultraviolet region which will be the topic of further investigations.

The compound obtained at pH 12 exhibits ionic characteristics [11] and is soluble in water, while the compounds containing two or one ethylenediamine ligands are insoluble in water. The structure of the anhydrous tetracyanocomplex compound containing two ethylenediamine ligands has been described in the literature [12]. The structure of $Ni(en)_2Ni(CN)_4 \cdot nH_2O$, which contains water, is being investigated in our department.

The compounds prepared in the acid region, especially those at pH 6 and 5, are interesting from the point of view of their sorptive properties. It has

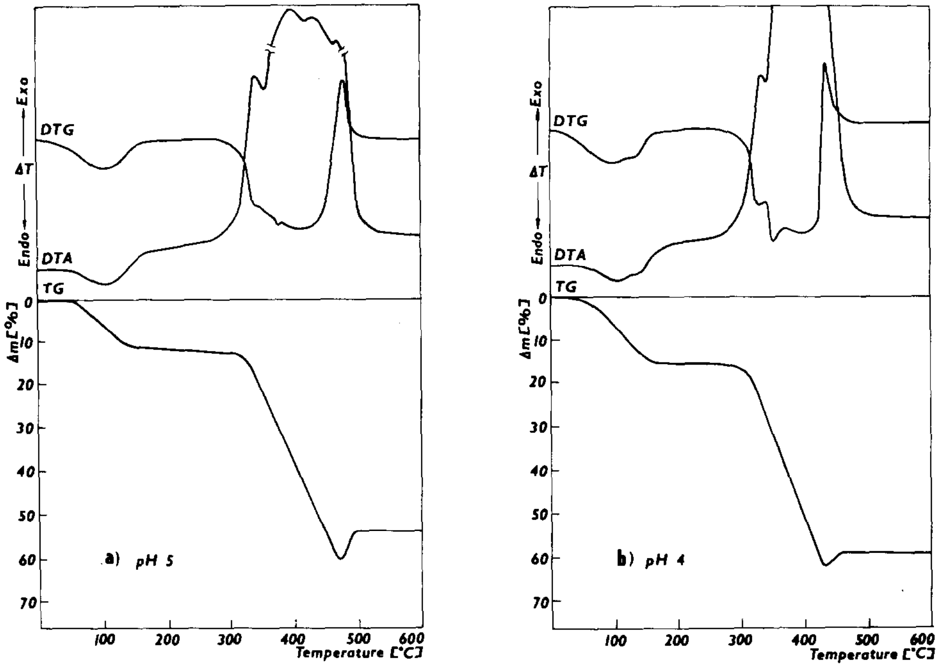

Fig. 4. TG, DTG and DTA curves of $Ni(en)Ni(CN)_4 \cdot nH_2O$: (a) pH 5, $n = 2$; (b) pH 4, $n = 2.7$.

been ascertained by measuring the infrared spectra, by CHN analysis and by gas chromatography that heating the compounds to 150 °C in order to yield an anhydrous product is followed by resorption of water from the surrounding atmosphere. The infrared spectra of the original compound and the compound after heating are almost identical. These facts as well as the results obtained using these compounds as a stationary phase in gas chromatography, [7,8] suggest their suitability for sorption processes.

The study of the influence of medium on composition and properties of the compounds having the general formula $Ni(en)_mNi(CN)_4 \cdot nH_2O$ ($m = 1$, 2 or 3 and $n > 0$) enabled the preparation of compounds with different numbers of ethylenediamine ligands and different water contents which differ in thermal stability and in which the guest component (H_2O) can be replaced by other organic compounds in different temperature intervals. In addition, for this type of compound (provided $m = 3$), H_2O may be replaced by different forms of iodine which interact with the host component (the ethylenediamine ligands). Because of this, a degree of electrical conductivity can be observed [13].

In this paper, we have demonstrated that the host component with varying ethylenediamine content or else in the form of different isolated products does not change by heating and is able to include the guest component.

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