

INCLUSION COMPOUNDS OF TETRACYANO COMPLEXES AND THEIR ELECTRICAL PROPERTIES

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The presence of iodine and iodide ions in tetracyanonickelates inclusion compounds with the general formula $\text{Ni}(\text{B})_m\text{Ni}(\text{CN})_4 \cdot n \text{H}_2\text{O}$ ($\text{B} = \text{NH}_3$ or ethylenediamine) changes the properties of these compounds. High frequency conductance measurements in the range of $10 - 10^5$ Hz show that the products with ethylenediamine ligands have a higher electrical conductivity than those with NH_3 ligands. The differences in the electrical properties between the compounds studied are mainly caused by chemical composition, structure and morphology.

Many types of inclusion compounds involving a host and a guest component are known. The present study is concentrated on the inclusion compounds of tetracyano complexes. The host component is formed by the tetracyano complexes, the guest component G by water or by an additional compound. They have the general formula $\text{Ni}(\text{B})_m\text{Ni}(\text{CN})_4 \cdot n \text{G}$, where B is NH_3 or ethylenediamine or another nitrogen or oxygen containing ligands.

In this work we want to include further guest components with different oxidation states in the space formed by the host component. We have tried to include iodine and its ions. The effect of iodine (in several oxidation states) on the properties of the host structure are unknown. The non-stoichiometry of the compounds (with respect to m and n), together with the polymeric structure¹ containing layers and cavities, may be very advantageous for these ions.

In order to synthesize compounds with the properties desired, we have applied knowledge about polymeric adducts of iodine², exhibiting different values of electrical conductivity and knowledge about compounds^{3,4} included with polyiodine anions ($\text{I}_2 \cdot \text{I}_3^-$, I_2 or I_5^- , I_5^- , I_5^- and others). The ability of the polyiodide anions to form chains could help us to elucidate the electrical properties and interactions in our new products.

EXPERIMENTAL

Preparation

Our starting compounds were $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ or $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (en = ethylenediamine) and iodine in the form of a I_2/KI solution or iodine in solid form⁵. The chemical composition of the starting tetracyano complexes is dependent on the pH; these effects are summarized in Tables I and II.

By changing the reaction conditions – the temperature and the nature and quantity of iodine (liquid I_2/KI or solid iodine) – we obtained several products differing in their content of included ions and equally in their properties (e.g. electrical conductivity).

The iodine and iodide contents depended on the composition of the tetracyanonickelate, on the nature and the quantity of iodine⁸ and on the shape and size of the ligands in the original tetracyanonickelate. The shape determines the accessibility of the interlayer space with the ethylenediamine more strongly intersecting the layers than the ammonia ligands.

Analysis

The compounds studied were identified analytically by IR spectroscopy (IR spectrometer Specord M80, Zeiss, Jena, Germany) and by thermal analysis (derivatograph MOM OD 102, Hungary). The iodine content was determined by the method of Schoniger. Iodine (and potassium) was also determined by Electron Probe Microanalysis (JXA-5A, JEOL) applying Kevex. Morphologies were studied using Scanning Electron Microscopy (JSM 840A, JEOL and for iodine free samples also JSM 35 CF, JEOL).

The chemical characteristics of the product obtained by the reaction between tetracyanonickelates and iodine are presented in Table III.

Electrical Measurements

The electrical properties of the original compounds and the products with iodine were studied by conductance and capacitance measurements with a Precise Capacitancy Bridge (General Radio 1616,

TABLE I
Results of elemental analyses and nickel determination in compounds $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ (I) and $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (II) refs^{6,7}

Compound	Calculated/Found			
	% C	% H	% N	% Ni
<i>I</i> ^a	16.58	3.40	29.00	40.52
	16.81	2.99	28.82	40.47
<i>II</i> ^b	28.61	6.24	33.36	27.97
	28.67	6.42	33.09	28.17

^a Prepared at pH 8. ^b Prepared at pH 12.

U.S.A.) in the range of $10 - 10^5$ Hz. Some of them were studied as a function of temperature in the range of 298 – 423 K. The temperature was controlled with 0.5 K accuracy (Chinoterm 10A, Hungary). The samples used for electrical measurements (200 mg) were pressed in the form of a disk (12 mm diameter, 1 – 2 mm thick). Graphite emulsions were used as electrodes.

TABLE II
Chemical analysis of $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n \text{H}_2\text{O}$ in dependence of the preparation conditions⁶

pH	<i>n</i>	Calculated/Found			
		% C	% H	% N	% Ni
9	0.5	17.91	2.86	32.41	43.81
		17.77	2.8	31.50	43.40
8	1.9 ^a	16.58	3.40	29.00	40.52
		16.81	2.99	28.82	40.47
7	2	16.48	3.45	28.82	40.26
		16.60	3.09	28.62	39.95
6	2.5	15.95	3.68	27.96	39.06
		16.40	3.1	28.27	39.00
5	4	14.66	4.3	25.65	35.84
		15.12	3.49	25.6	35.75

^a The compound *I* used in this work.

TABLE III
The chemical characteristics of the products obtained by the reaction between tetracyanonickelates $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ (*I*) or $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (*II*) and iodine⁸

Original sample		Product of the reaction with iodine						
No.	colour	No.	colour	% C	% H	% I	% N	% Ash ^a
<i>I</i>	Light blue	<i>IA</i>	light brown	13.37	2.38	20.98	18.09	42.36
<i>II</i>	Violet-pink	<i>IIA</i>	bright brick red	19.94	4.59	28.73	20.37	25.32
<i>II</i>	Violet-pink	<i>IIB</i>	bright brick red	14.72	3.24	44.56	16.65	20.19

^a The content of the ash residue found by the elemental analysis agrees with the sum of the nickel content found by the Electron Probe Microanalysis and complexometric analysis and the potassium content found by the Electron Probe Microanalysis.

RESULTS AND DISCUSSION

Our study concerns two inclusion compounds of tetracyano complexes: $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ and $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$, doped with iodine. In all products the colour changed (Table III) and the conductivity in the whole frequency range increased because of the presence of iodine in the inclusion compounds. In preliminary experiments^{5,8} the compounds containing ethylenediamine ligands exhibited higher conductivities, therefore, we paid more attention to them. The conductivity, σ , was dependent on the iodine content and on the synthetical conditions. For the products obtained by the reaction between $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ and an iodine solution σ ranged between 10^{-6} and $10^{-9} \text{ S cm}^{-1}$ at 298 K and frequency between 10 and 10^5 Hz .

Electron Probe Microanalysis (EPMA) confirmed the presence of iodine and potassium in these products. During the preparation of the I_2/KI solution addition of iodine to KI results in the formation of KI_3 and other polyiodide ions. According to the results of elemental analysis, IR spectroscopy, thermal analysis and EPMA, given in Table III, the composition of the products may be expressed by the general formula $\text{Ni}(\text{en})_m\text{Ni}(\text{CN})_4 \cdot x \text{I}_2 \cdot y \text{KI}_3 \cdot n \text{H}_2\text{O}$ with $2 < m < 3$, $0.1 < x < 1$, $0.1 < y < 1$.

The infrared spectra showed that the presence of iodine affects the ethylenediamine ligands of the host component. The m value changed from the original $m = 3$ to $2 < m < 3$. The changes in the vibrations, especially those of the NH_2 groups of ethylenediamine⁸ are more significant if the action of iodine on the compound is more intensive.

Upon reaction with iodine, the NH_2 group is supposed to join to the iodine as a new group: $-\text{C}=\text{N}^+-\text{H}$, to be found at $1\ 680 \text{ cm}^{-1}$, Fig. 1, similarly as stated in the case of the iodine adducts of nylon-6, also containing amino groups².

The band of $\delta(\text{NH}_2)$ at $1\ 145 \text{ cm}^{-1}$ weakens with increasing iodine content. Furthermore, changes were found in $\nu(\text{H}_2\text{O})$ ($3\ 570 - 3\ 400 \text{ cm}^{-1}$), $\nu(\text{NH}_2)$ ($3\ 350 - 3\ 250 \text{ cm}^{-1}$), $\delta(\text{H}_2\text{O})$, $\delta(\text{NH}_2)$ ($1\ 655 - 1\ 580 \text{ cm}^{-1}$), $\delta(\text{NH}_2)$ ($1\ 145, 1\ 010 - 970 \text{ cm}^{-1}$) and $\rho(\text{NH}_2)$ (at 700 cm^{-1}).

Dielectric studies^{9,10} of inclusion compounds provide some information about reorientation of the corresponding guest molecules. Also our recent results¹¹ about products containing zeolites, doped with iodine in a way analogous to that discussed here for the tetracyanonickelates, may provide information concerning the mode of iodine enclosure. In the zeolites the remaining water affected the effects of iodine. However, a more profound understanding of the effects of iodine, its ions and water in the space of the inclusion compounds studied here, requires to solve the structure, as it was done in the literature for some inclusion compounds^{9,10}.

The product of the reaction between $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ and an iodine solution containing 28.73% I (product IIA in Table III, 21.84% Ni, 2.95% K) was used to investigate the dependency of the conductivity on the temperature. The conductivity was measured as a function of frequency in the temperature range 298 – 423 K. The con-

ductivity increased with temperature. However, the conductivity as well as the capacity decreased at 421 K due to chemical transformations resulting from the start of the thermal decomposition (Fig. 2). Between 333 and 393 K water was lost. In the original compound $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ endothermic delibration of ethylenediamine occurred between 423 and 538 K with a maximum in DTA at 598 K. In product *IIA* only half of the water was lost in the first endothermic process below 421 K, and consequently the ethylenediamine delibration occurred at another value of m and therefore the temperature interval was shifted. Iodine and iodide (see the potassium content in Table III) interacts weakly with the tetracyanonickelate, manifested by a shift in the end of the thermal decomposition from 703 K for the original tetracyanonickelate to 763 or 823 K for its products.

At 298 K the conductivity depends on the frequency over three orders of magnitude. At 421 K the dependency was less significant. After cooling down to 298 K the con-

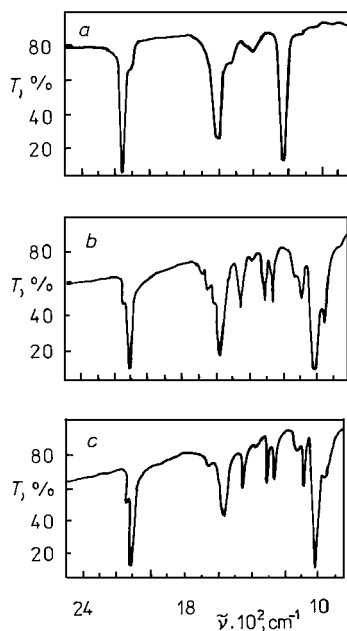


FIG. 1

IR spectra (transmittance T in %) of products doped with iodine prepared from: *a* $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ (20.98% I); *b* $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (28.73% I), product *IIA*; *c* $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (44.56% I), product *IIB*

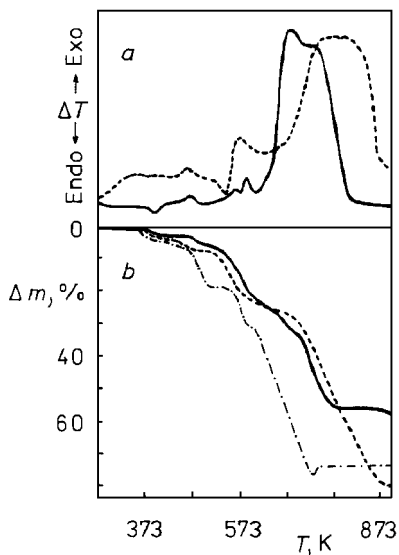


FIG. 2

Thermal analysis (DTA (a) and TG (b) curves) of product obtained from the reaction of $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$: — with iodine solution (28.73% I), powdered product *IIA*, - - - with solid iodine (42% I), crystalline product; - · - · - the original $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$

ductivity and capacity were both lower than measured previously, which can be a result of a partial thermal decomposition^{7,8}.

The complex impedance spectrum at 298 K has the shape of a semicircle (Fig. 3a) with the center shifted under the real axis. This is caused by a relaxation process in the conductivity with scatter about a single value for the relaxation time¹². In the low frequency part of the semicircle is distorted, suggesting that a second relaxation process exists, or the electrode–dielectric interface appears in this part of the plot.

At higher temperatures the spectra changed the shape. The character of the diagram at 328 K (Fig. 3b) indicates that the bulk conductivity increases and the electrode–electrolyte interface becomes effective¹³. The spectrum at 375 K is similar to that one at 328 K. Thermal analysis indicated that at 328 K decomposition products start to escape to a little extent. The TG curve of the thermal decomposition shows a discontinuity at 370 K (Fig. 2). The mass loss during this endothermic decomposition corresponds to 3% (water and a small percentage of the iodine escapes from the compound). The mass loss is not significant between 393 and 463 K. The products of the beginning of the

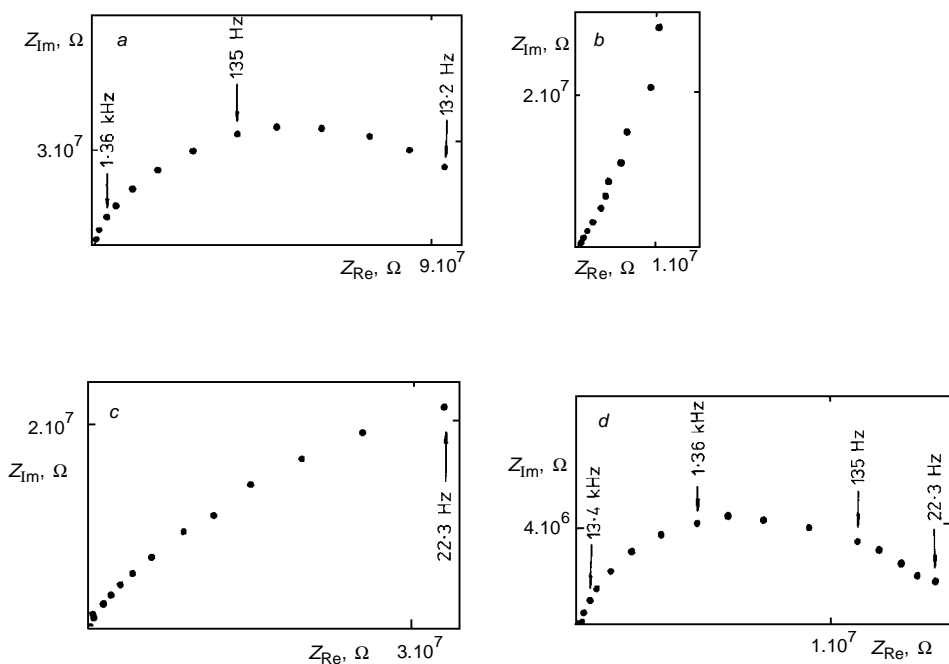


FIG. 3

Complex impedance plot of the product *IIA* obtained from the reaction of $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ with iodine solution (28.73% I). Measured at: *a* 298 K, *b* 328 K, *c* 398 K, *d* 421 K

thermal decomposition serve as carriers and are therefore able to change the conditions for conduction at the interface with the electrodes.

The conductivity of the sample is lower at 421 K than at 398 K. When the temperature is higher than 375 K, the impedance spectrum bends towards a semicircle (Fig. 3c and 3d). The impedance plot at 421 K (Fig. 3d) is again a semicircular arc with the center shifted below the real axis. The arc is deformed at low frequencies. The differences between the impedance spectra at 298 and 421 K on the one hand and at 328 and 398 K when the mass loss occurs on the other hand support the opinion that the products of the partial thermal decomposition contribute to the conductivity process.

The real and imaginary parts of the permittivity at 298 and 421 K (Figs 4a, 4c) show a frequency dependence characteristic for a hopping mechanism¹⁴. In Fig. 4b ϵ' and ϵ'' are given as a function of the frequency at 328 K. The effects of polarization are evident in the shape of the ϵ'' curve¹⁵.

The product investigated so far was a powderous sample. In order to solve the structure we prepared a crystalline product. This crystalline product was obtained under modified conditions by using solid iodine at 65 – 70 °C. At this temperature iodine reacted even as a vapor with the compound $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$. The structure of the

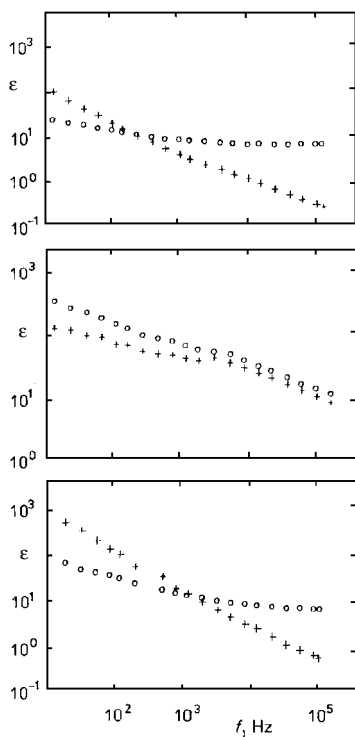


FIG. 4
The frequency dependence of the complex permittivity components of the product *IIA* obtained from the reaction of $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ with iodine solution (28.73% I). Measured at: *a* 298 K, *b* 328 K, *c* 421 K. \circ ϵ' , $+$ ϵ''

product has not been resolved yet. Naturally, the thermal decomposition of this product differed from previous results. The conductivity of the crystalline product was much smaller than for the powderous product.

The morphology of the powderous product containing ethylenediamine differed from the crystalline one. Figure 5 presents a scanning micrograph of the original compound $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (in crystalline form). During the reaction of this compound with iodine (solution) the iodine reacts mainly with the ethylenediamine ligands and in such a manner it interacts with the layers. The originally very regular bars forming the layers become irregular by the presence of the newly included guest, but their size remains similar in the powderous sample (Fig. 6). The crystalline reaction product with solid iodine contains a system of fibers. They are finer and their length has decreased (Fig. 7).

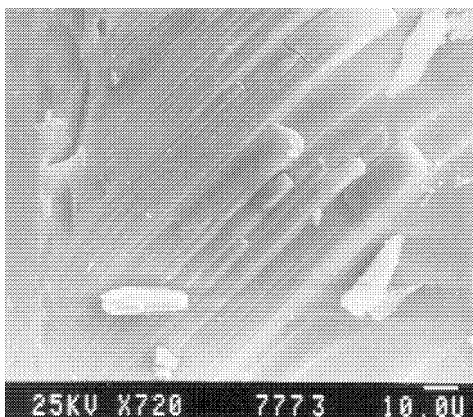


FIG. 5

Scanning electron micrograph of the original compound $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ in its crystalline form

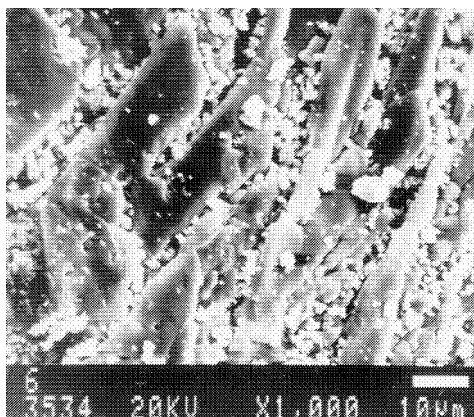


FIG. 6

Scanning electron micrograph of the compound $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ after reaction with iodine solution (44.56% I), powdered product *IIB*

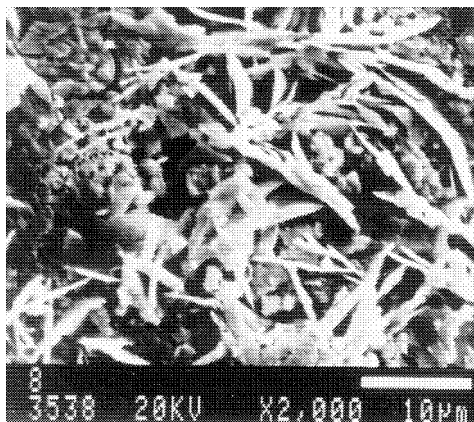


FIG. 7

Scanning electron micrograph of the compound $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ after reaction with solid iodine at the temperatures 338 – 443 °C (42% I), crystalline product

The space of the compound is filled with these small fibrous formations, the path ways are less accessible. It represents also a proof, that the reaction conditions during synthesis influence the morphology and the properties.

The second type of compound investigated was obtained by the reaction between the clathrate compound $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n \text{H}_2\text{O}$. ($n = 1.9$) and an iodine solution. The conductivity was between 10^{-8} and $10^{-10} \text{ S cm}^{-1}$ in the frequency range studied at 298 K. The original clathrate compound $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ without iodine exhibited values of $10^{-9} - 10^{-11} \text{ S cm}^{-1}$.

The essential features of the structure of the original compound are the layers of the tetracyano complexes in the host^{16,17}. The water molecules occur as guest between these layers, but also other molecules can be included between the layers. The $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n \text{H}_2\text{O}$ compounds are advantageous in sorption processes^{1,18}, because they are suitable to accept new guests. The compound with a non-stoichiometric amount of water was intentionally chosen for the synthesis of a product with iodine and iodide in the interlayer space. The structure is spatially more open for the movements of ions than that of $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$, because the ethylenediamine ligands are more protruding between the layers. The results with $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n \text{H}_2\text{O}$ were eventually worse, because the weaker NH_3 ligand can not interact with the iodine and therefore the presence of iodine has less influence on the electrical properties. The impedance spectrum of the product of the reaction between $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ and iodine solution *IA* (composition see Table III, 31.54% Ni, 4.70% K) comprises a semicircle with the center below the real axis (Fig. 8), but the deviations are small, indicating a single relaxation time.

The guest components in reaction products of this type may be water, iodine or iodide. The iodine in this type of product does not react with the less reactive ligands (NH_3) of the host, which has been confirmed by infrared spectroscopy⁸. These results are consistent with results of dielectric measurements in the literature⁹, where water as a guest has a weak interaction in the clathrate hydrate.

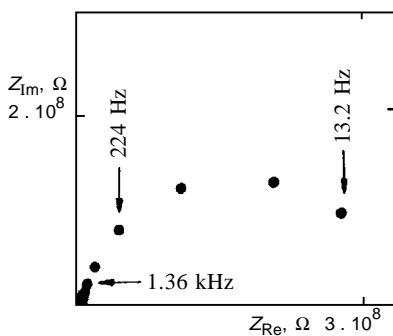


FIG. 8
Complex impedance plot of the product *IA* obtained from the reaction $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ with iodine solution (20.98% I). Measured at 298 K

The frequency dependence of the components of the relative permittivity at 298 K in Fig. 9 exhibits a form characteristic for hopping conduction¹⁴, similar to the previous compounds in Figs 4a and 4c.

The differences in electrical properties between the two types of compounds studied here are mainly due to their chemical composition and the different structures of the original compounds. Products containing ethylenediamine as ligand are capable to enclose higher amounts of iodine and its ions than the compounds containing NH_3 , which only weakly protrudes the layers of tetracyanonickelates. In the former case iodine and its ions actually react with ethylenediamine. In the latter case iodine is merely absorbed in the interlayer space, which is less separated by the B ligands. Therefore, no interaction was found between the NH_3 ligands and the iodine. In the case of ethylenediamine the space can be thought of as pillar shaped. An interaction with iodine may exist and is sometimes visible.

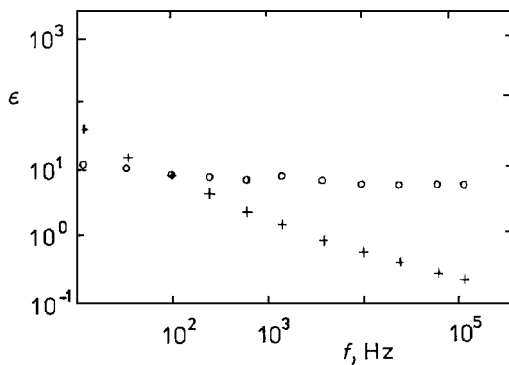


FIG. 9

The frequency dependence of the complex permittivity components of the product obtained from the reaction of $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 1.9 \text{H}_2\text{O}$ with iodine solution (20.98% I). Measured at 298 K. ○ ϵ' , + ϵ''

CONCLUSION

Depending on the character of the original host component, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n \text{H}_2\text{O}$ or $\text{Ni}(\text{en})_3\text{Ni}(\text{CN})_4 \cdot n \text{H}_2\text{O}$, iodine can either be just included in the available space in the inclusion compound, or it can interact with the ethylenediamine ligand present in the host component. This difference was demonstrated with electrical measurements, mainly with the values of σ , also in comparison with the original tetracyanonickelates.

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