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The Preparation of Tetracyanonickelates Showing Electrical Conductivity

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Abstract. The tetracyanonickelates $Ni(NH_3)_2Ni(CN)_4 \cdot 1.9\,H_2O$ (**1**), $Ni(NH_3)_{1.65}(C_4H_8O_2)_{0.2}Ni(CN)_4 \cdot 0.8\,C_4H_8O_2 \cdot 0.35\,H_2O$ (**2**) and $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (**3**) exhibit, after contact with a solution of iodine (I_2/KI), appreciable weight gains. According to thermal analysis, IR spectra and chemical analysis the new products contain intercalated iodine and iodides with the highest iodine content found in the product formed from (**3**). The results of high frequency conductance measurements of this product showed the highest value of electrical conductivity σ (10^{-6} S cm^{-1}). Other compounds show relatively low values of σ (10^{-8}–10^{-11} S cm^{-1}).

The iodine together with its iodide and polyiodide forms enters host (**3**) as an intercalated species. The iodide and polyiodide forms are formed during the initial redox reactions between the NH group of the ethylenediamine and the iodine.

Key words. Tetracyanonickelate, the products with iodine and iodides, electrical conductivity, clathrates.

1. Introduction

The clathrates of tetracyanocomplexes have been known for a long time [1–3]. Some of them are capable of exchanging the original guest component for other convenient organic compounds if some amount of the guest is present and as such they are useful as sorptive materials, particularly if they were modified with auxiliary organic solvents, e.g. with 1,4-dioxane before use. The auxiliary solvent can substitute not only (part or all of) the guest, but also the original base B [4] in the formula $M(B)_mM'(CN)_4 \cdot n$ G. The sorptive and separative properties have until now been the main areas of utilization of these compounds. In the present communication we intend to show a new property of these compounds.

According to the literature besides the known quasi one dimensional conductors (including CT compounds) such as potassium cyanoplatinate [5] and graphite compounds [6], many inorganic or organic materials [7] are used as materials in electrochemistry. Some of them as active materials for the cathode or anode respectively for the zinc–iodine and lithium–iodine solid electrolyte galvanic cells [8–10]. Some of them [10] are termed adducts, but some of them are also designated

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as inclusion compounds [5, 11, 12]. The compounds Li_xZrSe_2 [11] or Li_xZrNCl [12] are designated as intercalates (the lithium is accommodated between the layers) and they may be used as an electrochromic display (ECD electrodes).

Others such as tetra(*n*-butyl) ammonium triiodide $(n\text{-}C_4H_7)_4NI_3$ [13] or cyclodextrin (CD) polyiodides have as the guest component the iodine together with its polyiodide anions built in the cyclodextrin host. Their stoichiometry is: $(\alpha\text{-}CD)_2{\cdot}LiI_3{\cdot}I_2{\cdot}8\,H_2O$ or $(\beta\text{-}CD)_2{\cdot}KI_7{\cdot}9\,H_2O$ [14]. Sometimes the compounds have very different and varying chains of polyiodide anions alternating with molecular iodine. The sequence in the chain depends upon the extent of the redox reactions occurring between the iodine and some parts of the molecule forming the host.

In the present study our products suggest some analogy mainly with the cyclodextrin compounds (with different iodine forms intercalated). But we find some analogy also with the iodine adducts of Nylon-6 [10]. Pure iodine exhibits a high electrical resistance [10] and therefore the literature [9, 10] contains reports of attempts to prepare its adducts with electron donors. To increase the electrical conductivity in the case of our tetracyanocomplexes a higher occupancy of the voids in the host lattice is necessary. According to its IR spectrum, thermal behavior and diffraction patterns $Ni(en)_3Ni(CN)_4{\cdot}H_2O$ (**3**) is analogous to $Zn(en)_3Ni(CN)_4{\cdot}H_2O$ in which the water molecules are not bonded directly to the central metal atoms, but chains of $H_2O\cdots[Ni(CN)_4]^{2-}\cdots H_2O$ units along the *c*-direction [15] could be observed as a consequence of hydrogen bonding. The purpose is to have voids filled with a more heterogenous and more strongly varying mixture of the oxidation states of the iodine.

2. Experimental

2.1. PREPARATION

For the synthesis by the reaction with iodine we used the compounds: $Ni(NH_3)_2Ni(CN)_4{\cdot}1.9\,H_2O$ (**1**), $Ni(NH_3)_{1.65}(C_4H_8O_2)_{0.2}Ni(CN)_4{\cdot}0.8\,C_4H_8O_2{\cdot}0.35\,H_2O$ (**2**) and $Ni(en)_3Ni(CN)_4{\cdot}H_2O$ (**3**). The preparation and identification of compounds (**1**) and (**2**) have been described in previous publications [16, 17]. Compound (**3**) was prepared by mixing solutions of KCN (1.5 g KCN in 12.5 cm^3 H_2O) and $NiSO_4$ (3 g $NiSO_4{\cdot}7\,H_2O$ in 12.5 cm^3 H_2O). A precipitate of $Ni[Ni(CN)_4]{\cdot}n\,H_2O$ was obtained. The precipitate was dissolved in a 1 M solution of ethylenediamine (about 45 cm^3). Thus we obtained a violet solution in which immediately a violet-pink precipitate of the composition $Ni(en)_3Ni(CN)_4{\cdot}H_2O$ was formed. The precipitate was filtered, washed with a small amount of cold water and dried in a desiccator over silica gel.

The results of CHN analyses and nickel determination of compounds (**1**), (**2**) and (**3**) are given in Table I.

The products containing the iodine or iodides were prepared in the following way: 500 mg of the tetracyanonickelates (**1**), (**2**) or (**3**) were vigorously mixed in contact with 1 cm^3 of a 5% iodine solution (always in KI). The emulsion formed was allowed to stand (in air) for 1–2 days and then they were dried in a desiccator over silica gel. In the case of compound (**3**) a double quantity of iodine was used

Table I. Results of CHN analyses and nickel determination in compounds $Ni(NH_3)_2Ni(CN)_4 \cdot 1.9\ H_2O$ (**1**), $Ni(NH_3)_{1.65}(C_4H_8O_2)_{0.2} \cdot 0.8\ C_4H_8O_2 \cdot 0.35\ H_2O$ (**2**) and $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (**3**)

Sample	Compound	C(%) calc. found	H(%) calc. found	N(%) calc. found	Ni(%) calc. found
(**1**)	$Ni(NH_3)_2Ni(CN)_4 \cdot 1.9\ H_2O$	16.58	3.40	29.00	40.52
		16.81	2.99	28.82	40.47
(**2**)	$Ni(NH_3)_{1.65}(C_4H_8O_2)_{0.2}Ni(CN)_4 \cdot$				
	$0.8\ C_4H_8O_2 \cdot 0.35\ H_2O$	27.93	4.00	23.00	34.13
		27.68	4.00	23.16	34.23
(**3**)	$Ni(en)_3Ni(CN)_4 \cdot H_2O$	28.61	6.24	33.36	27.97
		28.67	6.42	33.09	28.17

(product **4I**). All samples showed a weight increase. The analyses of all the compounds are shown in Table II.

All starting compounds were analytical grade chemicals.

2.2. IDENTIFICATION OF PRODUCTS

The identification of the compounds was made by CHN analysis (Hewlett Packard CHN Model 185), nickel, iodine and potassium determination, thermal analysis and by recording the IR spectra. Nickel determination was made by complexometry and the potassium and iodine contents by Electron Microsonda measurements (JXA-5A, JEOL) applying Cevex. Parameters used: accelerating voltage 25 kV; sample current 1.5×10^{-7}A; analysing crystal LiF–PED. Iodine was also determined by the known method of Schöniger.

All TG, DTG and DTA analyses of the prepared compounds were measured up to 600°C in air on a Derivatograph MOM OD 102 (Paulik–Paulik–Erdey, Budapest) with the same conditions (weight of sample 100 mg; sensitivities: TG 100 mg, DTA 1/5, DTG 1/5; heating rate 6° $\min^{-1}$ and 9° $\min^{-1}$; reference material Al_2O_3).

The structure of the compounds was checked by the KBr disc technique using an IR spectrometer Specord M 80 (Carl Zeiss, Jena).

2.3. ELECTRICAL MEASUREMENTS

The electrical properties of the original and the iodine containing products were studied by the conductance and capacitance measurements on a General Radio Precision Capacitancy Bridge 1616 (U.S.A.) in the range 10–10^5 Hz at 25°C. The product (**3I**) was measured at various temperatures within the range 25 to 148°C. The temperature was stabilised by a Chinoterm 10 A (Hungary) controller with ±0.5°C accuracy. An emulsion of graphite was used as electrodes.

The samples used for the electrical measurements were in the form of a disc (Carl Zeiss, Jena) of 12 mm diameter and 1–1.5 mm thick (200 mg of sample) pressed at 65 kP cm^{-2}.

Table II. The products of the reaction of tetracyanonickelates with iodine

Original sample		Product of the reaction with iodine							
No.	Colour	No.	Colour	C(%)	H(%)	N(%)	Ni(%)	iodine(%)	K(%)
(1)	light blue	**(1I)**	light brown	13.37	2.38	18.09	31.54	20.98	4.70
(2)	violet-blue	**(2I)**	dark brown	17.26	2.29	21.24	29.10	17.05	4.35
(3)	violet-pink	**(3I)**	bright brick red	19.94	4.59	20.37	21.84	28.73	2.95
(3)	violet-pink	**(4I)**	bright brick red	14.72	3.24	16.65	17.30	44.56	2.69

(1) $Ni(NH_3)_2Ni(CN)_4 \cdot 1.9\ H_2O$
(2) $Ni(NH_3)_{1.65}(C_4H_8O_2)_{0.2}Ni(CN)_4 \cdot 0.8\ C_4H_8O_2 \cdot 0.35\ H_2O$
(3) $Ni(en)_3Ni(CN)_4 \cdot H_2O$

3. Results and Discussion

3.1. PREPARATION

Three types of tetracyanonickelate clathrates (**1**), (**2**) and (**3**) were prepared and identified, obtaining four products of their reaction with the solution of iodine (**1I**), (**2I**), (**3I**) and (**4I**). We found in all cases some definite weight gain, in a significant form in compounds (**3I**) and (**4I**), that is in good agreement with the results of the iodine determination (Table II). The sorbed quantities of iodine and iodides in the products depended directly on the quantity of the iodine used and of the KI used for the solubilisation and on the conditions of preparation.

3.2. THERMAL ANALYSIS

The derivatographic curves TG, DTA and DTG of the original compound [16] $Ni(NH_3)_2Ni(CN)_4 \cdot 1.9\ H_2O$ (**1**) and of the compound (**1I**), produced by the reaction of (**1**) with iodine, differ only up to 250°C. The change involves the liberation of iodine from the surface or from the interlayer space and the desorption of intercalated water. After further contact with water product (**1I**) regains its original light blue colouring and for this reason the presence of iodine in the structure of the host cannot be assumed.

When we compare the derivatographic curves of the compounds $Ni(NH_3)_{1.65}(C_4H_8O_2)_{0.2}Ni(CN)_4 \cdot 0.8\ C_4H_8O_2 \cdot 0.35\ H_2O$ (**2**) containing 1,4-dioxane [17] and of its product with iodine (**2I**) the aliquots of the originally present 1,4-dioxane (present as the guest component and also as ligand) after the reaction with iodine are released. This is checked also by the IR spectra of the intermediate product (controlled after heating to 150 and 360°C).

By the comparison of the derivatographic curves (Figure 1) of the products (**3I**) and (**4I**) with the original compound [18] $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (**3**) the change in the course of the thermal decomposition could be stated. Sample (**4I**) which is formed by the double aliquot of the used iodine solution shows also its more strongly affected thermal decomposition, which is caused by the presence of iodine.

3.3. IR SPECTRA

We found no striking differences in the IR spectra of the original compound (**1**) and of the product (**1I**) formed after the reaction with iodine. Only the vibrations νH_2O (3650–3550 cm^{-1}), δNH_3, δH_2O (1650–1550 cm^{-1}) and ρH_2O (650–550 cm^{-1}) were changed in their intensities against the original compounds [16].

The original compound (**2**) and its product (**2I**) formed by the reaction with iodine, exhibited weaker bands assigned to 1,4-dioxane for νCH_2 (2990–2850 cm^{-1}), δCH_2 (1450–1280 cm^{-1}), νCOC (1120–1110 cm^{-1} and 1040 cm^{-1}) together with the changes noted previously for (**1I**).

The original sample (**3**) and its products (**3I**) and (**4I**) showed some differences in their infrared spectra (Figure 2). The changes are in the bands; νH_2O (3570–3400 cm^{-1}), νNH_2 (3350–3250 cm^{-1}), δH_2O, δNH_2 (1580–1655 cm^{-1}), δNH_2 (1145, 970–1010 cm^{-1}) and ρNH_2 (at 700 cm^{-1}). We found a new frequency $\nu(C{=}N^+)$ (at 1680 cm^{-1}). Similar changes were found in the iodine adduct of

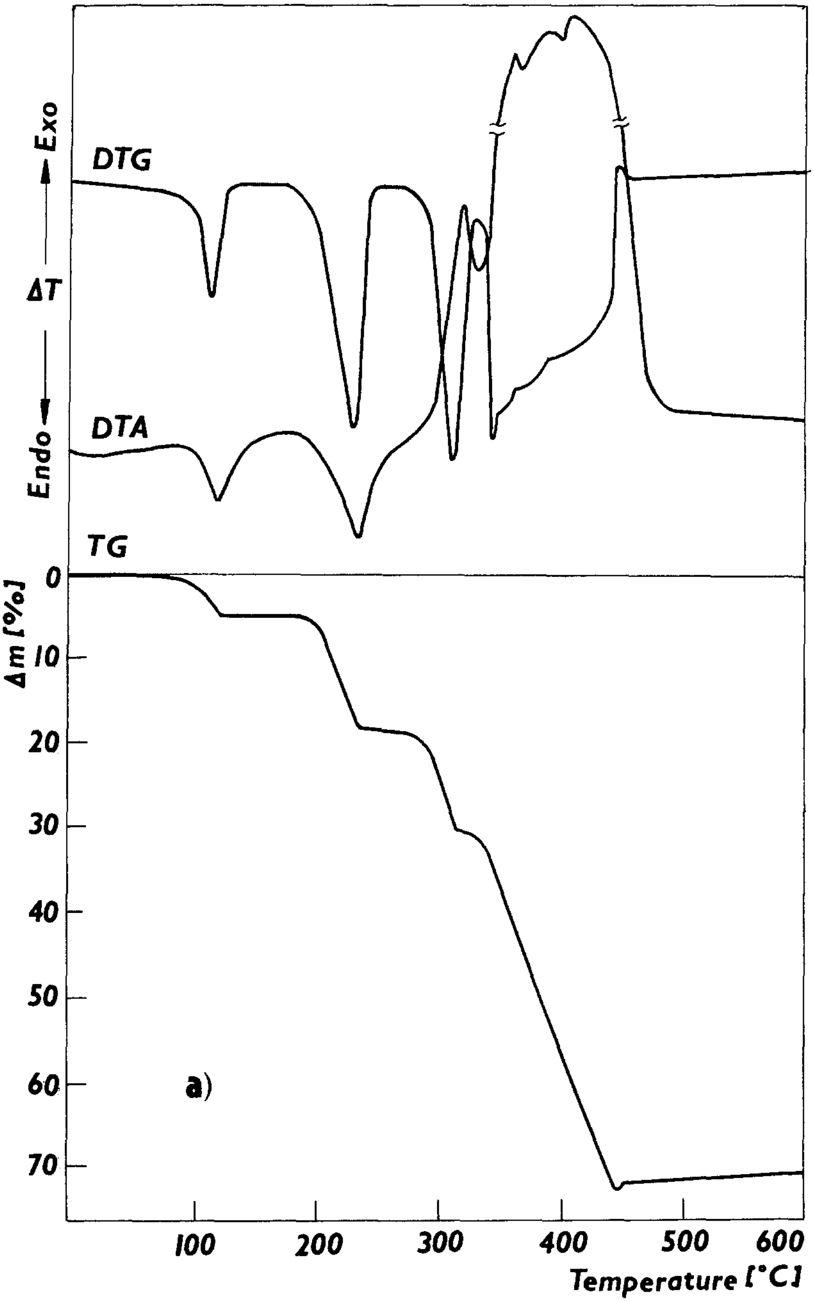

Fig. 1(a). TG, DTA and DTG curves of the compound $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (3).

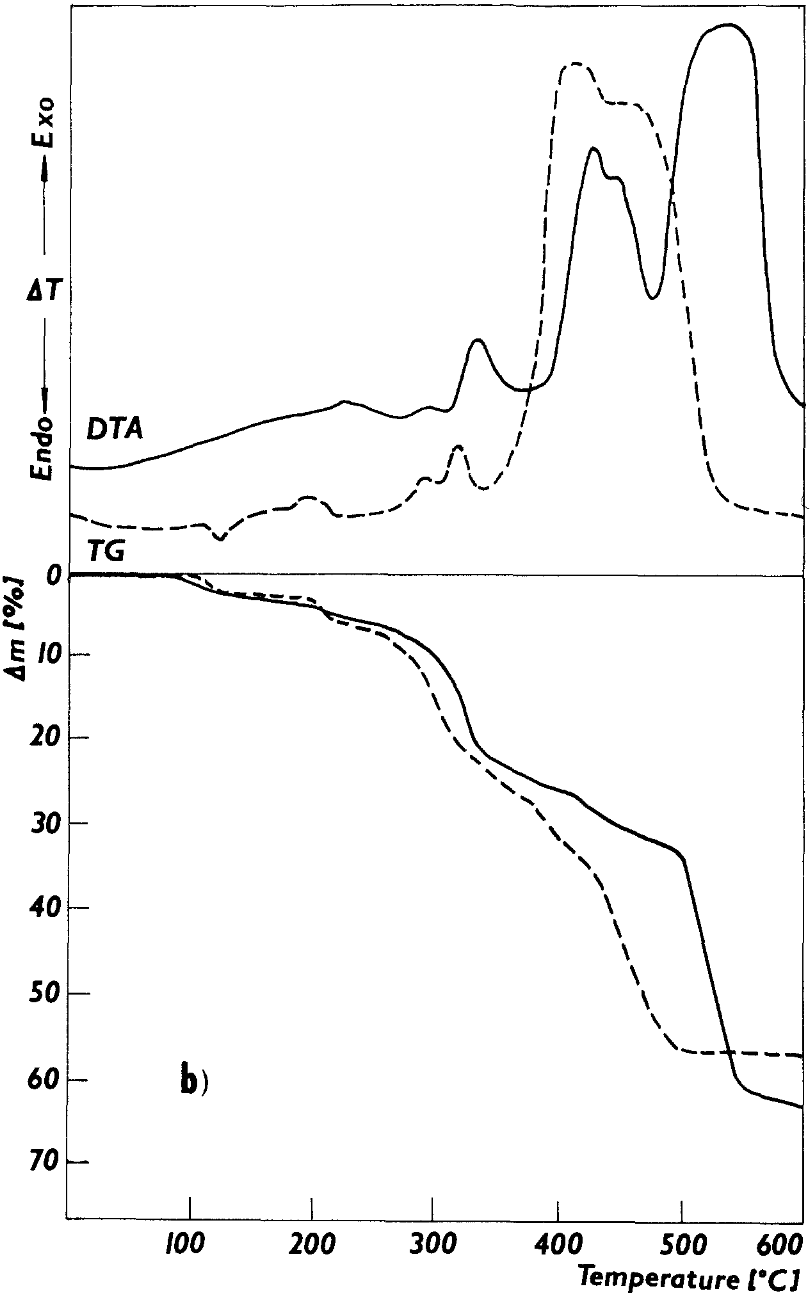

Fig. 1(b). TG and DTA curves of the compound $Ni(en)_3Ni(CN)_4{\cdot}H_2O$ after contact with the solution of iodine: ---- sample (3I), —— sample (4I).

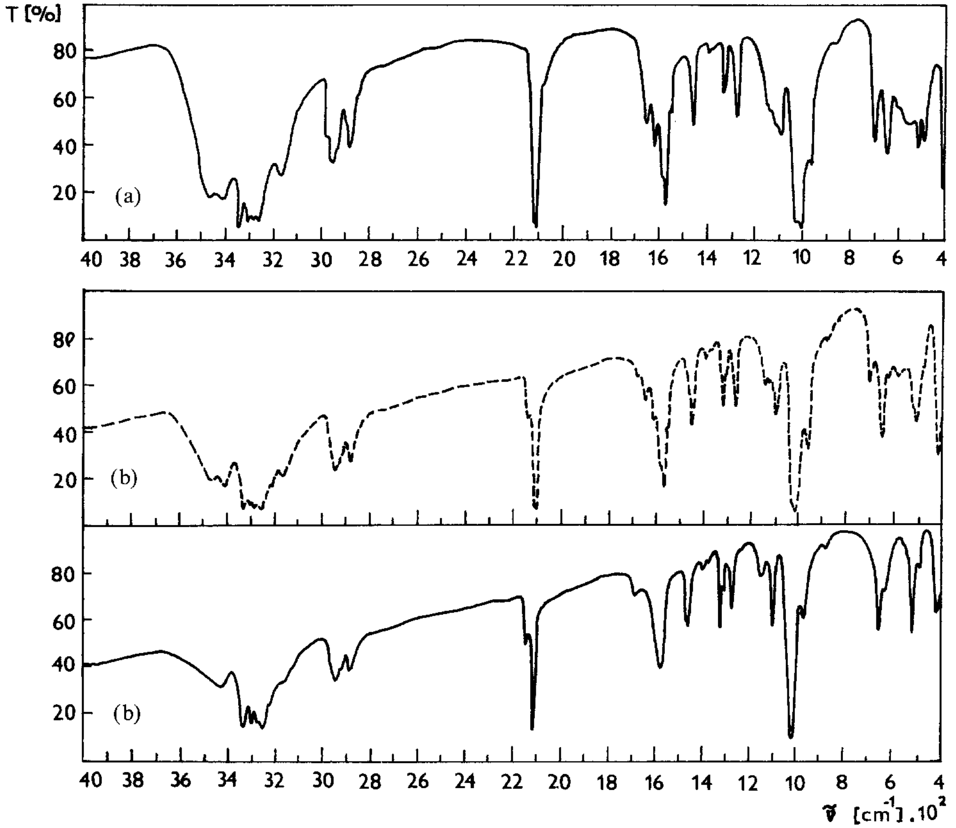

Fig. 2. The IR spectra of (a) the compound $Ni(en)_3Ni(CN)_4{\cdot}H_2O$ (**3**). (b) after contact with the solution of iodine: ---- sample (**3I**), —— sample (**4I**).

Nylon-6, which result from the interaction of iodine and NH_2 and in such manner a new group $>C{=}N^{+}<^{H}$ joined to the iodide ions was formed [10]. According to [19] a band in the region 2200–1800 cm^{-1} may also be assigned to the same group (2150 cm^{-1} for (**3I**) and (**4I**)). According to the IR spectra (Figure 2) in compound (**4I**) the changes are more evident.

3.4. ELECTRICAL MEASUREMENTS

All products produced by the reaction with the solution of iodine (**1I**), (**2I**), (**3I**) and (**4I**) exhibited a higher value of the electrical conductivity over the whole range of frequencies used (10–10^5 Hz, at 25°C). The dependence of the electrical conductivity on the frequencies is given in Figure 3.

The sample (**3I**) was studied also in the temperature interval 25–148°C.

We found the highest value in the case of the product of reaction of $Ni(en)_3Ni(CN)_4{\cdot}H_2O$ (**3**) with iodine-compounds (**4I**) and (**3I**), the former also has

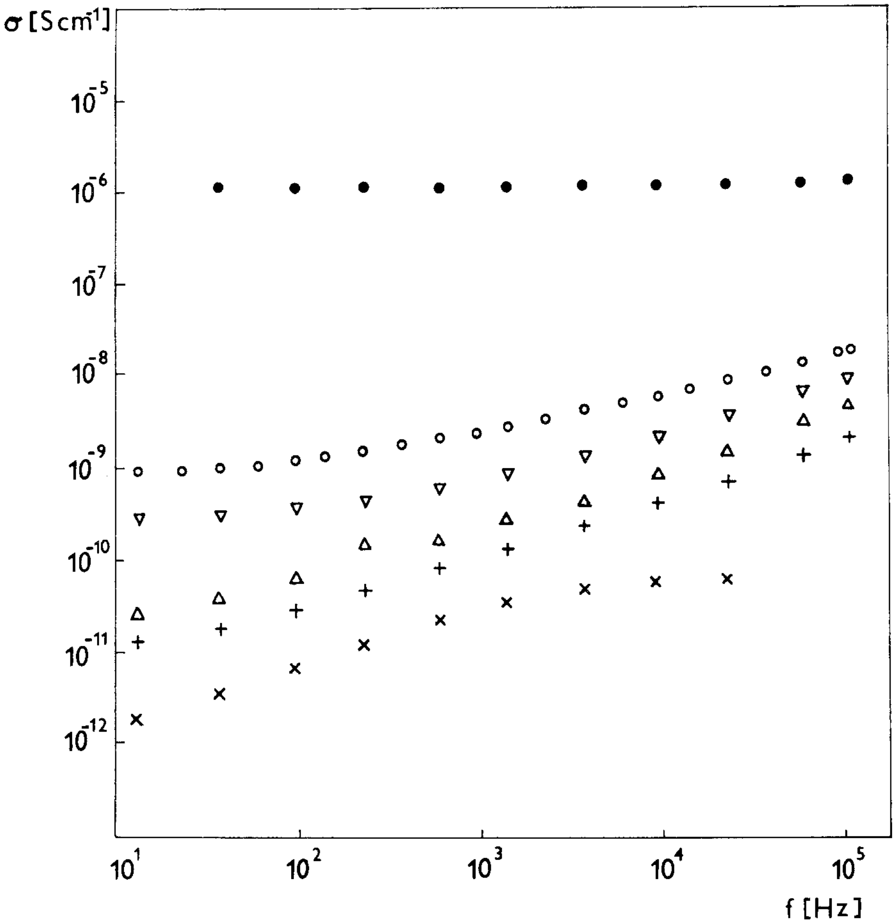

Fig. 3. The frequency dependence of the electrical conductivities (at 25°C). Compound used: △ (**1**); ▽ (**1I**); ×(**2**); +(**2I**); ○ (**3I**); ● (**4I**).

the highest content of iodine for all the compounds. In the case of (**1I**) and (**2I**) the iodine content was relatively low, therefore equally the values of electrical conductivities are low.

The frequency dependence of the complex permittivity components exhibits (Figure 4) at 25°C the shape characteristic of hopping conductivity [20]. The value of the relative permittivity is stabilised at higher frequencies. The values of the relative permittivities (ε_r) measured at 25°C and 106.6 kHz are summarised in Table III.

The complex impedance plots of compounds (**1I**) and (**3I**) measured at 25°C (Figure 5) exhibit a typical circular form with the center displaced below the real axis. We assume that this represents a relaxation process with the relaxation times around one value of the relaxation time [21].

In the case of the product (**3I**) the shape of the complex diagram changed with increasing temperature. At 55°C it is characteristic of a purely resistive shorting

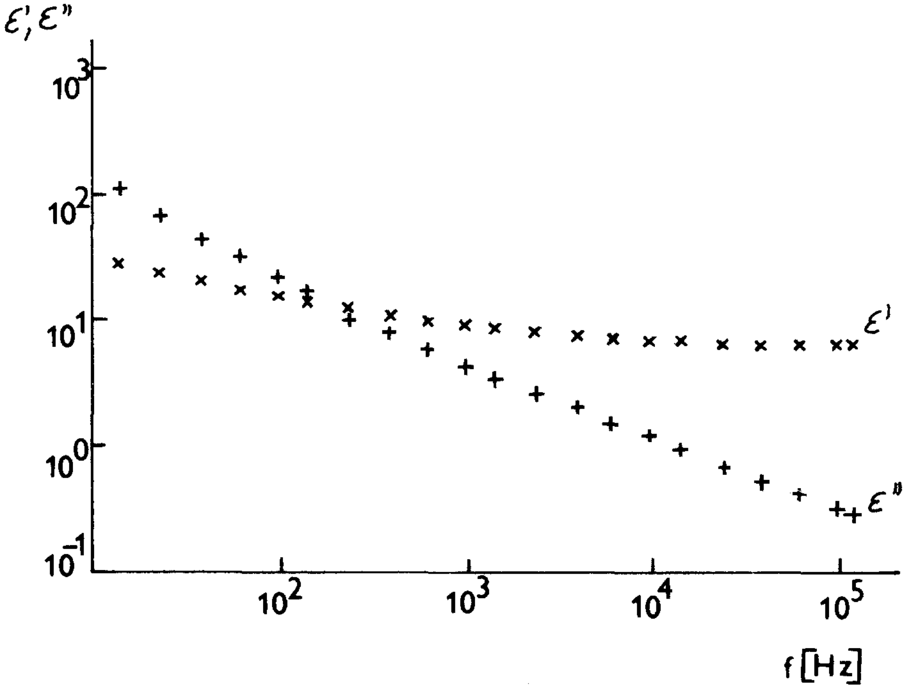

Fig. 4. The frequency dependence of the components of the complex permittivity for product (**3I**).

path [22]. The characteristic plot is not well defined, possibly due to the electrolyte–electrode effects.

The results of the electrical measurements with inclusion compounds of tetracyanonickelates are the first and as such their properties are not known from the literature. But they show that the compound (**4I**) – the product of the reaction of iodine with $Ni(en)_3Ni(CN)_4 \cdot H_2O$ – exhibited a medium electrical conductivity (σ) of magnitude 10^{-6} S cm^{-1} (Figure 3). The inclusion of iodine in the tetracyanonickelates is not known from the literature and this value of σ could not result from the presence of iodine alone because this exhibits a high electrical resistance [10].

Table III. The values of the relative permittivity (ε_r) for the studied samples (at 25°C, 106.6 Hz)

Sample	ε_r
(**1**)	5.4
(**1I**)	5.0
(**2**)	1.9*
(**2I**)	3.5
(**3I**)	6.7
(**4I**)	7.9

* Measured at 22.4 kHz.

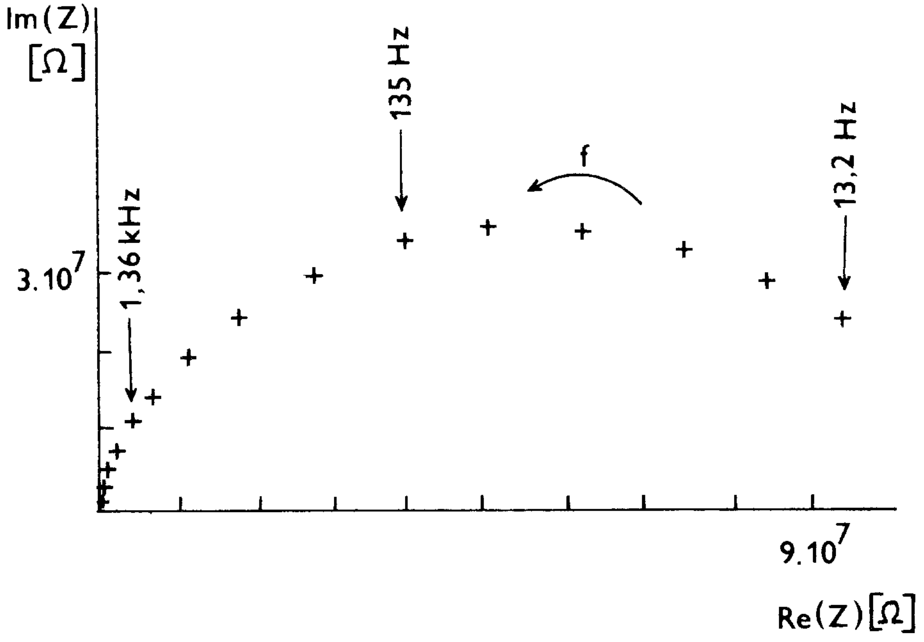

Fig. 5. Complex impedance plot using the sample (**3I**), measured at 25°C.

The samples obtained by the reaction with the solution of iodine (I_2/KI) exhibited in all compounds higher values of σ than the original compounds. Samples (**1I**) and (**2I**) have the electrical conductivity of magnitude 10^{-11}–10^{-8} S cm^{-1} and sample (**3I**) has 10^{-9}–10^{-8} S cm^{-1} (at 25°C, in the studied frequencies range).

But values in the same range (about 10^{-9} S cm^{-1}) are similar to those measured by Yamamoto [10] in the case of the iodine adducts of Nylon-6, which equally contained less than 60% of iodine. Further compounds prepared by these authors [9, 10] which according to them exhibited a medium electrical conductivity (10^{-7}–10^{-3} S cm^{-1}) were used as the active materials in lithium–iodine solid electrolyte galvanic cells, especially at a load of high electrical resistance (e.g. 500 kΩ).

We may propose for compounds (**3I**) and (**4I**) according to the analytically determined components the chemical compositions: $\mathrm{Ni(en)}_m\mathrm{Ni(CN)_4{\cdot}0.4\,KI_3{\cdot}0.5\,H_2O}$ for compound (**3I**) and $\mathrm{Ni(en)}_m\mathrm{Ni(CN)_4{\cdot}0.5\,KI_3{\cdot}0.4\,I_2{\cdot}0.4\,H_2O}$ for compound (**4I**), where $2 < m < 3$. Therefore we may presume in the proposed forms of these compounds that the iodine and iodides are intercalated between the layers.

In the case of these products we found that the new guests may interact with the surrounding ligands of the host (containing N—H group). The extent of the interaction may be quantified only if the structure of the product (**4I**) could be elucidated, but the present product (**4I**) exists in a powder state. For comparison we prepared also a crystalline form of compound (**3**) containing iodine, whose structure is now being studied.

The tetracyanonickelates without the presence of iodine exhibit only non significant values of the conductivity σ (Figure 3). Only their doping with iodine makes them potential conductors.

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