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$\{[NiL][Co(NCS)_4]\}_n$, an organic–inorganic coordination polymer (L = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)

Spectroscopic, magnetic and thermal characterization

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Bretsznajder Special Chapter

Abstract The organic–inorganic coordination polymer of the general formula $\{[NiL][Co(NCS)_4]\}_n$ (where L = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has been synthesized and characterized by IR, UV–Vis, DSC/TG, DTA/TG/MS methods. The magnetic behaviour of this complex has also been investigated within the temperature range 1.8–300 K. The IR spectrum indicates the presence of bridging M–NCS–M′ ligands. The absorption bands of UV–Vis spectrum confirm that the coordination environment of nickel(II) ions changes from square planar for $[NiL](ClO_4)_2$ to octahedral for $\{[NiL][Co(NCS)_4]\}_n$. The obtained compound is stable at room temperature, but within the range 246–282 °C decomposes in a three-stage process. The first step is associated with decomposition of the coordination polymer to the cationic $[NiL]^{2+}$ and anionic $[Co(NCS)_4]^{2-}$ units; the next two stages correspond to gradual decomposition of the macrocyclic ring. The value of molar magnetic susceptibility ($\chi_M T = 2.16\ \mathrm{cm^3\ mol^{-1}\ K}$) indicates that the compound is paramagnetic.

Keywords Organic–inorganic coordination compound · $[Co(NCS)_4]^{2-}$ units · Spectroscopic properties · Thermal decomposition · Magnetic behaviour

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Introduction

Heterometallic coordination compounds comprise a still growing proportion in current research of the chemistry of coordination combinations. Particularly interesting are coordination complexes containing bridging ligands between metal centres. The studies on heterometallic coordination complexes focus most of all on determination of exchange interactions between central ions (as for magnetic properties) as well as analysis of the electronic structure and depiction of electron transitions (spectroscopic properties) [1–4].

Such compounds of special interest include heterometallic systems obtained based on metal complexes with organic ligands and salts being derivatives of Prussian blue $[M(CN)_6]^{n-}$, (where $M = Cr^{III}, Fe^{III}, Mn^{III}, Fe^{II}, Co^{III}, n = 3, 4$), which exhibit interesting magneto-structural properties [5–8]. Thiocyanate salts, in common with cyanate salts, can serve as bridging groups [9]. Usually applied ligands are macrocyclic Schiff bases [10]. Application of macrocyclic Schiff base ligands permits one to ‘plan’ the electronic structure of the central metal ion via selection of a proper geometry of coordination environment which directly affects magnetic properties of a compound. Research is also conducted into the thermal properties of this kind of compounds [11–13].

This article presents the results of a study on synthesis, thermal behaviour and magnetic and spectroscopic properties of an organic–inorganic compound of $\{[NiL][Co(NCS)_4]\}_n$, where L denotes 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The compound belongs to a group of so-called molecular magnets, i.e. a modern material which can compete with the conventional inorganic magnets. Its advantages include, among others, a low density, usually water solubility, and interesting electric/optical/structural properties. Such hybrid organic–inorganic compounds have recently been of great interest for their promising practical applications, for instance, in electronics, optics, pharmacy and environment protection.

To synthesize the $\{[NiL][Co(NCS)_4]\}_n$ coordination polymer, a semi-finished product of Ni^{2+} ion complex with an organic tetraaza macrocyclic ligand $[NiL](ClO_4)_2$ was applied. The latter metal complex was synthesized in this laboratory and, prior to the synthesis of the coordination polymer, characterized by the spectroscopic (IR, UV–Vis) and thermoanalytic (DSC/TG) techniques.

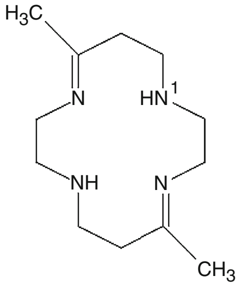
Experimental

Materials and synthesis

The following reagents, commercially available, were applied without additional purification: anhydrous ethylenediamine, methyl-vinyl ketone (for synthesis), chloric(VII) acid (analytically pure), nickel(II) acetate tetrahydrate (98%), KSCN, $CoCl_2 \cdot 4H_2O$ (pure) and the solvents ether, methanol, acetonitrile (analytically pure). The synthesis of the macrocyclic ligand (L) and its nickel(II) cation complex $[NiL](ClO_4)_2$, which were necessary for the synthesis of the coordination polymer of interest, was made by employing a modified version of the technique described in [14, 15]. The $[NiL](ClO_4)_2$ semi-finished product was then used for synthesizing the coordination polymer $\{[NiL][Co(NCS)_4]\}_n$.

Synthesis of the 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydrogen chlorate(VII) [L]

Chloric(VII) acid (70%, 0.036 mol) was introduced by drops into the 10% methanol solution of anhydrous ethylenediamine at −10 °C. During adding the acid, the solution was maintained at about −20 °C. Then, a newly prepared methanol solution of methyl-vinyl ketone (0.030 mol) at the 1:1 volume ratio was added by drops for 30 min and stirred until a precipitate had appeared. Stirring was still continued at a temperature of −15 °C for about 4 h. The obtained solution was left until it had got room temperature. The precipitate was filtered, flushed with methanol and diethyl ether, dried and stored at about 5 °C. The reaction yield was 32%. Molecule structure of the ligand is given below:



Synthesis of the 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) dichlorate(VII) [NiL](ClO$_4$)$_2$

The above macrocycle [L] (1.75 mmol) was mixed with the 10% methanol solution of nickel(II) acetate (1.75 mmol), heated and kept at boiling point for 2 h. Next, the solution was left until it had been cooled. The precipitate was filtered and flushed with cold methanol. The filtrate was evaporated to a small volume in order to obtain an extra amount of the product. The reaction yield was 80%.

Synthesis of the {[NiL][Co(NCS)$_4$]}$_n$ polymer L = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene

A 10 ml aqueous solution of KSCN (0.3 mmol) was added to 10 cm^3 of aqueous solution of $CoCl_2 \cdot 4H_2O$ (0.075 mmol). The obtained solution was introduced dropwise into 25 ml of acetonitrile solution of $[NiL](ClO_4)_2$ (0.15 mmol) at room temperature. The obtained green precipitate was filtered, flushed with diethyl ether and dried at room temperature. The reaction yield was 94%.

The composition of the obtained compounds, $[NiL](ClO_4)_2$ and $\{[NiL][Co(NCS)_4]\}_n$, was confirmed by elemental analysis (C, H, N, S) and ICP-AES (Ni and Co).

Experimental methods

The mid-infrared absorption spectra (MIR) were measured at room temperature using a Bruker Vertex 70 spectrometer in the 4000–400 cm^{-1} spectral range. KBr pellets were applied to measurements for the infrared range.

Polycrystalline infrared absorption spectra were measured with a Biorad 575C Fourier transform infrared (FTIR) spectrometer using KBr pellets in the 2000–400 cm^{-1} region. The temperature-dependent spectra within the temperature range of interest were measured using a helium-flow Oxford cryostat. Both room-temperature IR and temperature-dependent IR spectra were recorded with a spectral resolution of 2 cm^{-1}.

The UV–Vis spectrum was recorded with a CARY 500 Varian spectrophotometer in the spectral range of 200–900 nm from the powder sample pressed between two quartz plates.

Magnetization measurements at a magnetic field of $B = 0.5$ T in the temperature range 1.8–300 K were performed using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The SQUID magnetometer was calibrated with the palladium rod sample of the magnetic susceptibility 5.25×10^{-6} cm^3 g^{-1} ($T = 298$ K).

Thermal analyses were carried out using TG/DSC Setsys TM 1500 (Setaram) calorimeter under flowing argon (scanning rate 3 K min^{-1}, platinum crucibles, sample weight 0.001–0.020 g) up to 350 °C. In addition, the Netzsch STA 449F1/F3 TG/DTA/DTG thermoanalyzer (heating rate 5 K min^{-1}, alumina crucibles) coupled with the QMS 403 Aëolos quadrupole mass spectrometer (QMS 403C) via heated adapter under Proteus Software was used to characterize the products of decomposition. Mass range was 1–300 u and detection limit $>2 \times 10^{-14}$ mbar. The quartz-glass capillary was used as an interface between thermoanalyzer and QMS. Experiments were done in the 20–350 °C temperature range.

Results and discussion

The [NiL](ClO$_4$)$_2$ complex, as obtained using the above described procedure, was a yellow-orange colour. Spectroscopic investigations have confirmed its structure [16]. FTIR spectrum exhibits a number of absorption bands originated from atomic vibrations of atom groups in a big macrocyclic ring. The relevant frequency range are ν_s and ν_{as} (N–H) ≥3100 cm^{-1}; ν_s and ν_{as} (CH$_3$) and (CH$_2$) 2870–2980 cm^{-1}; ν (C=N) 1650 cm^{-1}; δ_{as} (–CH$_3$) and (=CH$_2$) 1400–1470 cm^{-1}; δ_s –CH$_3$) and ρ (=CH$_2$) 1370 cm^{-1}; ρt (=CH$_2$) 1300–1370 cm^{-1}; ν_{as} (C–N) 1050–1270 cm^{-1}; ν_s (C–N) and (C–C) 900–980 cm^{-1}. Absorption vibration bands of chlorate(VII) ions in the ranges ν_{as} (ClO$_4$)$^-$ 1120–1040 cm^{-1}, ν_s (ClO$_4$)$^-$ 928 cm^{-1} and δ (ClO$_4$)$^-$ 640–450 cm^{-1} are also visible (Fig. 1a).

At 470 nm, a band appears in the UV–Vis spectrum, which corresponds to *d–d* transitions of the Ni^{2+} ion. The band is typical of nickel(II) complexes having a square planar geometry and a d^8 electron configuration of the central atom [14]. The coordination environment of nickel ions suggest that, according to crystal field theory, unpaired electrons are lacking in the electronic structure of the central ion. Hence, it can be assumed from spectroscopy investigations that a compound with such structure should be a diamagnetic material.

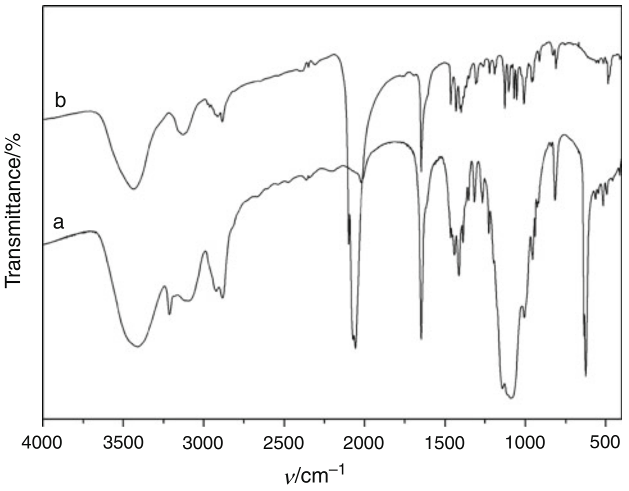
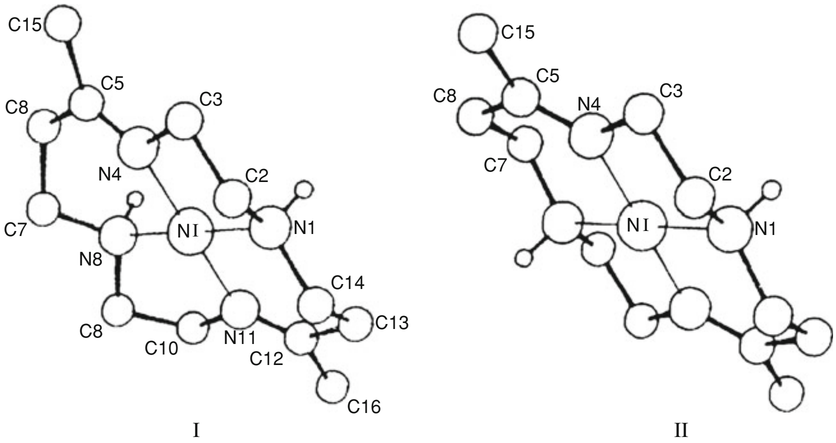


Fig. 1 FTIR spectra of [NiL](ClO$_4$)$_2$ (*a*) and {[NiL][Co(NCS)$_4$]}$_n$ (*b*)

According to [16], two isomeric forms of the macrocyclic ring, *cis*- (**I**) and *trans*- (**II**), of the ligand L are formed during the synthesis (Fig. 2). These forms differ in the location of the amino hydrogen atoms relative to the plane of the ring. Crystallographic studies [16], though, showed no significant differences in structure of both compounds. As those authors declare, the coordination environment of the Ni^{2+} ion in the *trans*- form is strictly planar, while the *cis*-configuration exhibits a small tetrahedral distortion of the coordination sphere of the central ion. However, during the synthesis described above, the *cis*- form is privileged and formed with a yield of 99%, and the 1% only for the *trans*- form [15]. Taking this into account, a mixture of ligand isomers was used to synthesize the [NiL](ClO$_4$)$_2$ complex, without the separation of isomers.

Thermal behaviour of the [NiL](ClO$_4$)$_2$ was studied by the TG/DSC technique in an inert atmosphere due to the

Fig. 2 Stereoviews of [NiL](ClO$_4$)$_2$ complexes [16]



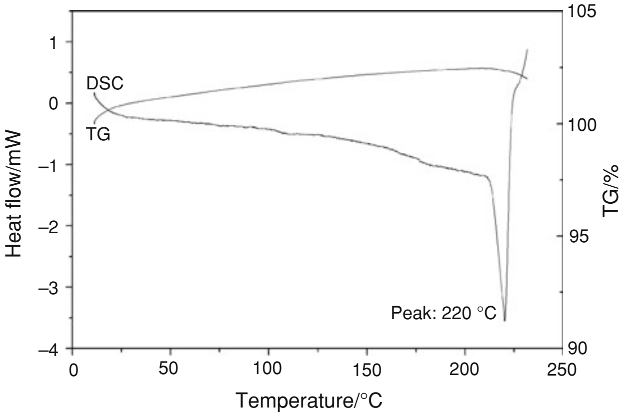


Fig. 3 DSC and TG curves of $[NiL](ClO_4)_2$; sample mass $m = 17$ mg

possibility of explosive decomposition of the complex (due to the presence of the ClO_4^- anions in the compound structure). Figure 3 shows DSC and TG curves of this complex as recorded during heating in an argon atmosphere. This complex is stable up to the melting point 214/220 °C (onset/peak). A strong endothermic effect which is present on the DSC curve corresponds to the melting process. The calculated enthalpy of the process is 22.5 J g^{-1} (10.9 kJ mol^{-1}). A small mass loss appears on the TG curve at the melting onset point (214 °C), which amounts to about 0.5% at 250 °C. It can be connected with changes in structure of the compound that are visible on the TG curve at melting point and/or in evaporation of the liquid.

To answer the question, temperature-dependent IR spectra were taken over the range 20–230 °C. The recorded *T*-FTIR spectrum of the compound (Fig. 4) indicates that during heating the changes occur in the bands ascribed to vibrations of chlorate(VII) ions, which start at 140 °C.

An isolated $(ClO_4)^-$ ion has nine normal modes, which are represented by four bands in an IR spectrum at frequencies $\nu_3 = 1119$ cm^{-1}, $\nu_1 = 928$ cm^{-1}, $\nu_4 = 625$ cm^{-1} and $\nu_2 = 459$ cm^{-1}. Splitting of the ν_2 (doubly degenerate), and ν_3 and ν_4 (triply degenerate) bands are observed due to symmetry reduction from the perfect configuration and crystal field effects. The ν_1 vibration frequency appears as a weak signal, in contrast to that such vibration is forbidden in infrared range [17, 18].

The vibration bands of chlorate(VII) ions have occurred at the frequencies $\nu_3 = 1113$ and 1052 cm^{-1}, $\nu_1 = 928$ cm^{-1}, $\nu_4 = 638$ and 625 cm^{-1} and $\nu_2 = 459$ cm^{-1}. It is seen from Fig. 4 that, during heating, the degeneration of ν_3 and ν_4 bands is partially abandoned with the accompanying gradual disappearance of ν_1 vibration band. Based on the spectroscopy data for the $(ClO_4)^-$, $(ClO_3)^-$ and $(ClO_2)^-$ ions [19], one can suppose the gradual decomposition of the chlorate(VII) ions by the chlorates(VI) and (IV) leading to chlorides. According to Nakamoto [19], reducing the symmetry of chlorate ions is accompanied by lifting of the ν_3 band degeneration and disappearance of the ν_4 band for the $(ClO_2)^-$ ions. Thus, for the obtained *T*-FTIR spectrum, the revealed changes should correspond to the decomposition process of the chlorate(VII) anions without any change in structure of the ring itself.

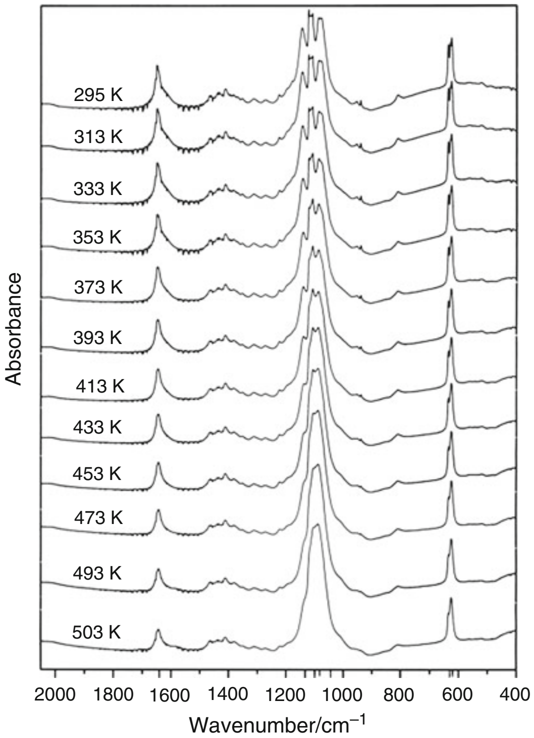


Fig. 4 Temperature-dependent IR spectra of $[NiL](ClO_4)_2$

A slight mass loss appearing on the TG curve only at 214 °C (Fig. 3) may indicate that the changes in $[NiL](ClO_4)_2$ structure, which are reflected in the *T*-FTIR spectrum at 140 °C, correspond to equilibrium. The supposition is confirmed by the equilibrium mechanism of the decay as given by [20]:

$$ClO_4^- \leftrightarrow ClO_3^- + O$$

$$ClO_3^- \leftrightarrow ClO_2^- + O$$

$$ClO_3^- \leftrightarrow 3/4ClO_4^- + 1/4Cl^-$$

$$ClO_2^- \leftrightarrow ClO^- + O$$

$$ClO_2^- \leftrightarrow 2/3ClO_3^- + 1/3Cl^-$$

$$2ClO^- \leftrightarrow Cl_2 + O^{2-} + O$$

Figure 1b presents a spectrum of the $\{[NiL][Co(NCS)_4]\}_n$ obtained from the reaction of $[NiL](ClO_4)_2$ with the cobalt chlorate ($CoCl_2{\cdot}4H_2O$) and KSCN. There is evidence for the production of the coordination polymer in the nickel–cobalt system: the observed changes in FTIR spectrum (Fig. 1) include the disappearance of bands attributed to vibrations of chlorate(VII) ions, and the appearance of a strong band at 2099 cm^{-1} which should correspond to vibrations of the thiocyanate structure. According to the Nakamoto's [19] criteria for identifying the SCN$^-$ ion bond in chemical complexes, the presence of the bridging thiocyanate group is manifested by the appearance of an stretching vibration band *v*(CN) at about 2100 cm^{-1} in an IR spectrum. The 2099 cm^{-1} band is split, which gives evidence of bidentate thiocyanate groups in the coordination complex. The presence of the thiocyanate group is confirmed also by the bands about 800 cm^{-1} (*v*(CS)). As it is in the case of a nickel(II) ion complex with a macrocyclic ligand, numerous bands attributed to a microcyclic ring's vibrations are observed in the IR spectrum. The related frequencies do not significantly change during creation of the coordination polymer (Fig. 1a, b).

The electronic spectra of the {[NiL][Co(NCS)$_4$]}$_n$ coordination polymer (Fig. 5) consists of the *d–d* type bands from different ions of the two metals with their different symmetry and the CT transition bands. A broad band at 474 nm corresponds to *d–d* transitions of a nickel ion, which is typical of nickel complexes having a square planar geometry [14]. Hence, the extra band at 594 nm might be due to a change in coordination of nickel from square planar ([NiL](ClO$_4$)$_2$) to octahedral ({[NiL][Co(NCS)$_4$]}$_n$) as a result of thiocyanate group coordination. This band partially overlaps with the band of *d–d* transitions of a cobalt ion located at about 630 nm. The proposed structure of the obtained {[NiL][Co(NCS)$_4$]}$_n$ coordination polymer is shown in Fig. 6. The polymeric chain of such a bimetallic compound is assembled of the units of [NiL] cations and [Co(NCS)$_4$] anions and, in addition, the [NiL] units alternate with the [Co(NCS)$_4$] units.

The thermal behaviour of the {[NiL][Co(NCS)$_4$]}$_n$ was studied by the TG/DSC techniques during heating in an argon atmosphere. As can be observed on DSC curves in Fig. 7, the polymer is stable to a temperature ca. 240 °C: there are not any thermic effects related to phase transformations, and the TG curve does not show any mass loss for the compound in question. During further heating, DSC reveals three endothermic effects with their peaks at 246, 273 and 282 °C and the onset at 232, 269 and 275 °C, respectively, but the first strong effect is not accompanied by a mass loss on the TG curve. The next two endothermic effects are connected with a gradual mass loss as recorded on TG curve, which loss amounts to about 10 wt% in the temperature range of 269–275 °C. It is assumed that the first endothermic effect is related to decomposition of the coordination polymer into cationic [NiL]$^{2+}$ and anionic [Co(NCS)$_4$]$^{2-}$ entities, whereas the next two effects are connected with the decay of the macrocyclic ring.

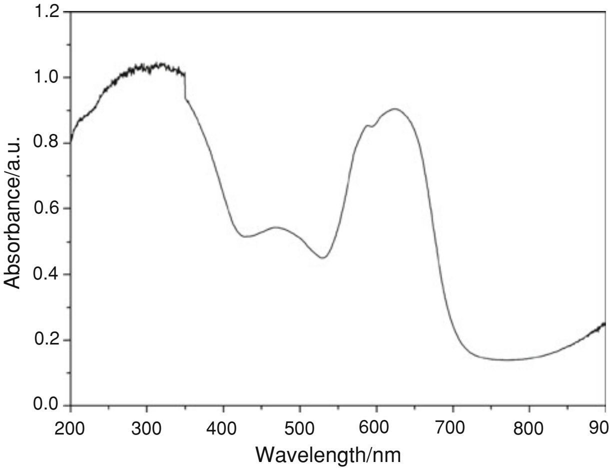


Fig. 5 Reflectance spectra of {[NiL][Co(NCS)$_4$]}$_n$

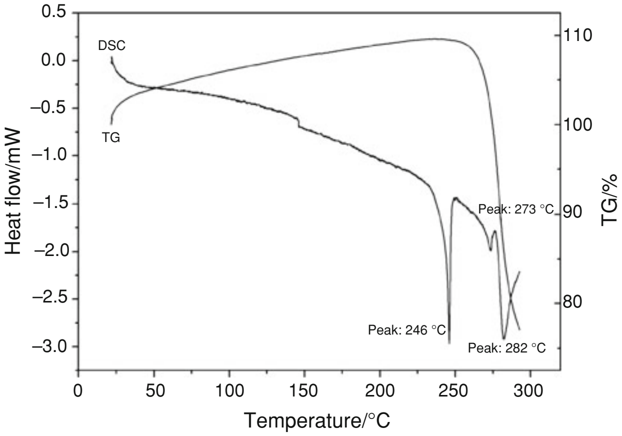


Fig. 7 DSC and TG curves of {[NiL][Co(NCS)$_4$]}$_n$; sample mass $m = 5$ mg

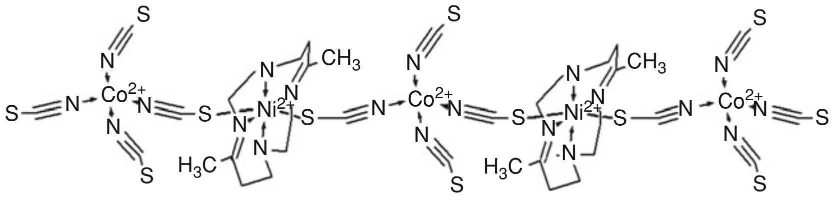


Fig. 6 Proposed structure of coordination polymer {[NiL][Co(NCS)$_4$]}$_n$

Conventional thermoanalytic studies such as TG/DTA/DSC do not allow for identification of gaseous products. For this reason, the TG/DTA/DSC coupled with MS techniques were employed to identify the products of decomposition and fragmentation of the $\{[\mathrm{NiL}][\mathrm{Co(NCS)}_4]\}_n$. It has been found that the decomposition is very complicated and proceeds in a temperature range. The polymer undergoes a stepwise decomposition during heating, to form various intermediate components, which results from the observed changes in structure, breakage of macrocyclic ring bonds and those within the thiocyanate ligands together with separation of the coordination bonds. Moreover, a number of species appear almost at the same temperature points.

Results obtained by the TG/DTA–MS techniques (Fig. 8) show that the polymeric structure of the complex decomposes first into the components $[\mathrm{NiL}]^{2+}$ and $[\mathrm{Co(NCS)}_4]^{2-}$. This is reflected by the small ion current signals which have been recorded for the mass-to-charge ratio related to a cationic unit of *m/e* equal to 142, and an ionic unit of 145 at the temperature about 150 °C. The process occurs with no change in TG curve.

In the first stage of decomposition (the first endothermic effect) at a temperature of 256/277 °C onset/peak recorded are the current signals from the ions whose *m/e* values amount to 64 and 26. These values can be ascribed to the ions $[\mathrm{SO}_2]^+$ and $[\mathrm{CN}]^+$, respectively. The ions can be originated from decomposition of the thiocyanate group. The presence of the $[\mathrm{CN}]^+$ ions may suggest the occurrence of the microcyclic ring's decomposition as well. This is confirmed by MS signals with *m/e* values of 16, 15, 14, 13 and 2 which can be ascribed to the ions $[\mathrm{NH}_2]^+$, $[\mathrm{CH}_3]^+$, $[\mathrm{CH}_2]^+$, $[\mathrm{CH}]^+$ and $[\mathrm{H}_2]^+$, respectively. These ions appear already at the first stage of decomposition, at 256 °C, but their amount considerably increases starting at 286 °C (the second endothermic effect 286/292 °C onset/peak). The situation can be explained by the ring's gradual degradation. First, the macrocyclic ring may be depleted of methyl groups, which is accompanied by breaking the single bonds C–N in the ring. At a higher temperature, a complete destabilization of the ring structure occurs with its decomposition into simple ions. The above process is accompanied by a mass loss of about 20%.

It should be noted that the changes in structure of the coordination polymer in the argon atmosphere (as recorded on the DSC/TG curves) start at a temperature by about 30 °C lower than that in the air (the TG/DTA–MS curves), but the TG recorded mass loss during the TG/DTA–MS (in-the-air) measurement is twice as high. The presence of air in the system TG/DTA–MS during thermal analysis may catalyze reactions which proceed during heating (by the oxygen reacting with SCN, which leads to creation of SO_2). This is in accordance with the mass spectrum data showing the presence of the molecular mass $\mathrm{SO}_2{}^+$ (*m/e* = 64). The decomposition process does not cease at 350 °C, but proceeds, which is suggested by the TG curve shape.

Magnetic field measurements by SQUID (Fig. 9) have shown that the compound has a value of molar magnetic

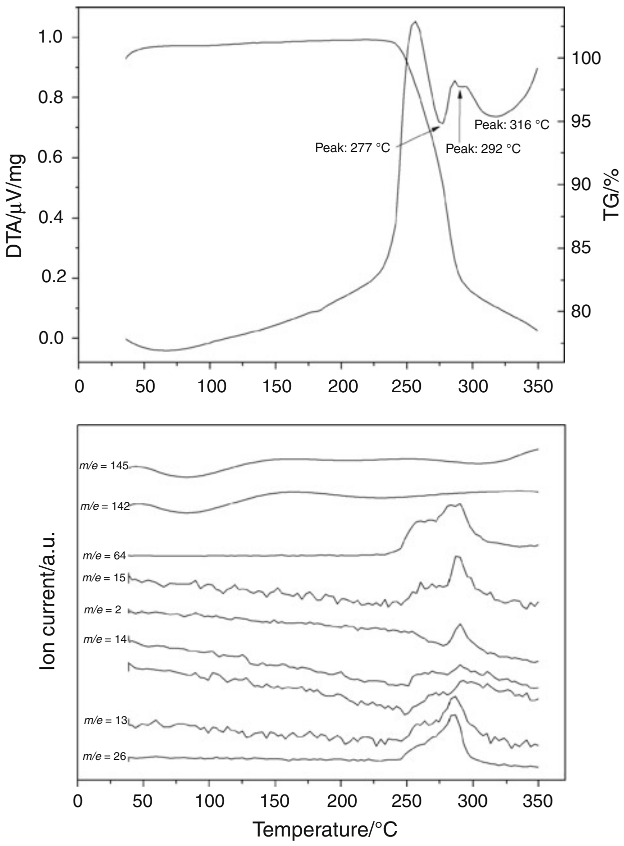


Fig. 8 TG/DTA–MS curves of $\{[\mathrm{NiL}][\mathrm{Co(NCS)}_4]\}_n$ (air atmosphere)

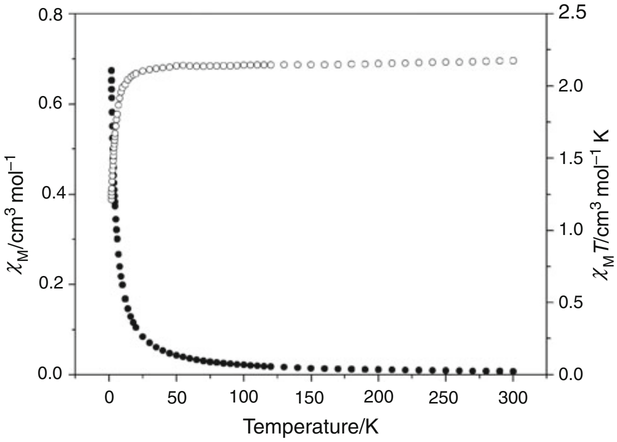


Fig. 9 The magnetic data χ_{M} (*closed circle*) and $\chi_{\mathrm{M}}T$ (*open circle*) versus temperature for $\{[\mathrm{NiL}][\mathrm{Co(NCS)}_4]\}_n$

susceptibility $\chi_M T = 2.16$ cm^3 mol^{-1} K (4.16 MB). The value is lower than that calculated for isolated metal ions of Ni^{2+} with $S = 1$ and Co^{2+} with $S = 3/2$, which is equal to 2.86 cm^3 mol^{-1} K (4.79 MB). This means that the compound is paramagnetic, for whom interactions can occur between the central ions. The $\chi_M T$ value does not change over a wide temperature range, although below 50 K a rapid fall is observed to be 1.21 cm^3 mol^{-1} K (3.12 MB) at the temperature 1.8 K. The reason for that lowering is mainly anisotropy typical of the tetrahedral ion Co^{2+} and the occurrence of parameter of zero-field-splitting.

The compound complies with the Curie–Weiss law in almost the whole temperature range (i.e. between 12 and 300 K). The calculated Curie and Weiss constants are $C = 2.16$ cm^3 mol^{-1} and $\theta = -1.18$ K, respectively. The negative small value of the Weiss constant can indicate superexchange interactions occurring via thiocyanate bridges as well as the occurrence of very weak antiferromagnetic interactions in the crystal lattice.

Conclusions

An organic–inorganic coordination polymer of general formula $\{[NiL][Co(NCS)_4]\}_n$, where L denotes 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene was synthesized by solution reaction among $[NiL](ClO_4)_2$, $CoCl_2{\cdot}4H_2O$ and KSCN. Spectroscopic and magnetic properties and thermal behaviour of the obtained compound were characterized. Also, we investigated the spectroscopic properties (MIR and UV–Vis) and thermal behaviour (DSC/TG) of the $[NiL](ClO_4)_2$ coordination compound, which was a semi-finished product in the $\{[NiL][Co(NCS)_4]\}_n$ synthesis. The FTIR and UV–Vis results confirm the $[NiL](ClO_4)_2$ structure and the DSC/TG data show that it is stable up to the melting point 220 °C. IR spectrum of the organic–inorganic coordination polymer indicates the presence of bridging M–NCS–M′ ligands, and the UV–Vis spectrum confirms that the coordination environment of nickel(II) ions is octahedral. The experimental magnetic data indicate that the compound is paramagnetic at room temperature ($\chi_M T = 2.16$ cm^3 mol^{-1} K). The dependence of $\chi_M T$ versus T suggests anisotropy characteristic of the tetrahedral coordination of Co(II) ions and/or the occurrence of the parameter of zero-field splitting. This study has shown that the compound of interest is stable at room temperature, but within the 243–280 °C temperature range decomposes in a three-stage process. The first step is associated with the decomposition process of the coordination polymer to the cationic $[NiL]^{2+}$ and anionic $[Co(NCS)_4]^{2-}$ entities, the next two stages correspond to the gradual decomposition of the macrocyclic ring. It is also found that the decomposition process is more intensive in the air atmosphere and the mass loss is twice as much as in argon.

References

1. Cristóvão B, Kłak J, Miroslaw B, Mazur L. Synthesis, crystal structures and magnetic characterization of heterodinuclear $Cu^{II}Gd^{III}$ and $Cu^{II}Tb^{III}$ Schiff base complexes. Inorg Chim Acta. 2011;378:288–96.
2. Mroziński J, Kłak J, Kruszyński R. Crystal structure and magnetic properties of the 1D bimetallic thiocyanate bridged compound: $\{(CuL_1)[Co(NCS)_4]\}$(L1 = *N*-rac-5,12-Me$_2$-[14]-4,11-dieneN$_4$). Polyhedron. 2008;27:1401–7.
3. Bieńko A, Kłak J, Mroziński J, Kruszyński R, Bieńko DC, Boča R. Rhenium(IV)–copper(II) heterobimetallic complexes: synthesis, crystal structure and magnetic properties. Polyhedron. 2008; 27:2464–70.
4. Wyrzykowski D, Kruszyński R, Kłak J, Mroziński J, Warnke Z. Synthesis and magnetic characteristics of new tetrachloroferrates(III) with 2-methylpyridinium, 3-methylpyridinium and 4-methylpyridinium cations: X-ray crystal structure of 4-methylpyridinium tetrachloroferrate(III). Inorg Chim Acta. 2007;360: 3354–60.
5. Mondal N, Saha MK, Mitra S, Gramlich V, Salah M. Synthesis, characterization and crystal structure of cyano-bridged dinuclear copper–iron. Polyhedron. 2000;19:1935–9.
6. Nemec I, Herchel R, Boča R, Svoboda I, Trávníček Z, Dlháň L, Matelková K, Fuess H. Heterobimetallic assemblies of Ni(II) complexes with a tetradentate amine ligand and diamagnetic cyanidometallates. Inorg Chim Acta. 2011;366:366–72.
7. Karadağ A, Şenocak A, Önal I, Yerli Y, Şahin E, Başaran AC. Preparation, structural, magnetic and thermal properties of two heterobimetallic cyano-bridged nickel(II)–copper(II)/platinum(II) coordination polymers. Inorg Chim Acta. 2009;362:2299–304.
8. Shevchenko DV, Petrusenko SR, Kokozay VN, Tomkiewicz A, Kłak J, Mroziński J, Krasovska MV, Shishkin OV, Linert W. Synthesis, crystal structure and magnetic properties of a 1D mixed-metal-mixed-ligand Ni(II)/Fe(II) coordination polymer built on the nitroprusside anion. Inorg Chim Acta. 2007;360: 2846–50.
9. Bieńko A, Kłak J, Mroziński J, Domagała S, Korybut-Daszkiewicz B, Woźniak K. Magnetism and crystal structures of $Cu^{II}Mn^{II}$ and $Cu^{II}Ni^{II}$ ordered bimetallic chains. Polyhedron. 2007;26: 5030–8.
10. Shebl M. Synthesis, spectral and magnetic studies of mono- and bi-nuclear metal complexes of a new bis(tridentate NO_2) Schiff base ligand derived from 4,6-diacetylresorcinol and ethanolamine. Spectrochim Acta A. 2009;73:313–23.
11. Zeybek B. Meltem Ates B, Ercan F, Levent Aksu M, Kılıc E¸ Atakol O. The effect of ligand basicity on the thermal stability of heterodinuclear Ni^{II}–Zn^{II} complexes. J Therm Anal Calorim. 2009;98:377–85.
12. Olar R, Badea M, Marinescu D, Lazar V, Chifiriuc C. New complexes of Ni(II) and Cu(II) with Schiff bases functionalised with 1,3,4-thiadiazole: spectral, magnetic, biological and thermal characterisation. J Therm Anal Calorim. 2009;97:721–7.
13. Gaber M, Rehab AF, Badr-Eldeen DF. Spectral and thermal studies of new Co(II) and Ni(II) hexaaza and octaaza macrocyclic complexes. J Therm Anal Calorim. 2008;91:957–62.
14. Kolinski RA, Korybut-Daszkiewicz B. Isomeric 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecanes and their nickel(II)complexes. Bull Acad Polon Sci Ser Sci Chim. 1969;17:13–8.
15. Kolinski RA, Korybut-Daszkiewicz B. Macrocyclic ligands and their metal ion complexes. Part VI. preparation, stereochemistry and conformational analysis of polyalkyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorates. Inorg Chim Acta. 1975;14:237–45.

16. Gluzinski P, Kolinski RA, Krajewski JW, Andreetti GW, Bocelli G. X-ray structural investigation of N-epimeric, 1,8-*cis*- and 1,8-*trans*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorates, $C_{12}H_{24}N_4Ni(ClO_4)_2$. J Crystallogr Spectrosc Res. 1991;21:145–51.
17. Marchewka MK, Drozd M, Pietraszko A. Structure, spectra and phase transition in *p*-nitroanilinium perchlorate crystal. Mater Sci Eng B. 2003;100:225–33.
18. Briget Mary M, Umadevi M, Pandiarajan S, Ramakrishnan V. Vibrational spectral studies of L-methionine L-methioninium perchlorate monohydrate. Spectrochim Acta A. 2004;60:2643–51.
19. Nakamoto K. Infrared and Raman spectra of inorganic and coordination compounds Part A. Theory and applications in inorganic chemistry. 6th ed. New York: Wiley; 2009.
20. Solymosi F, Raskó J. Study of thermal decomposition of some transition metal perchlorates. J Therm Anal. 1977;11:289–304.