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Kinetic, Spectroscopic and Magnetic Properties of 1,4,8,11-Tetraazacyclotetradecanenickel Bi- and Trivalent Complexes

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Nickel(II) and nickel(III) complexes of formula $[Ni^{II}LCl_2]$ and $[Ni^{III}LCl_2]^+$ containing tetraaza macrocyclic ligands with nitrogen donor atoms, where L = [14]aneN$_4$ (L^1), 2-Me[14]aneN$_4$ (L^2), 5,12-Me$_2$[14]aneN$_4$(L^3), 5,7,7,12,14,14-Me$_6$[14]aneN$_4$ (L^4), form stable crystals with a pseudo-octahedral geometry of central atom. This work concerns the methyl analogues of Ni(II) and Ni(III) complexes. Magnetic and spectroscopic measurements gave values of spectroscopic parameter g and paramagnetic temperature dependence characteristic for this type of compounds. Their properties were investigated using EPR, reflectance spectroscopy and IR techniques. The Faraday method was used for the investigation of magnetic susceptibility between 4.2–300 K.

Key words: Ni(II, III) complexes, EPR and IR spectroscopy, tetraazamacrocyclic complexes, electron transfer process, kinetic, magnetic and spectroscopic measurements

Bivalent $[Ni^{II}LCl_2]$ and trivalent nickel complexes $[Ni^{III}LCl_2]X$, X = Cl^-, ClO_4^-, containing tetraaza macrocyclic ligands having saturated nitrogen donors have been known and their chemical and physical properties have been investigated [1,2] as well as their structure [3]. Those complexes are especially interesting because of their importance in biological systems [4,5] and catalytic oxidation reactions [6,7]. Both nickel ions form exceptionally stable crystals with an octahedral geometry of Ni(II) and Ni(III) surround and a square-planar array of four nitrogens and two Cl^- anions occupying the axial positions [3]. The nickel(II) high-spin complexes with a d^8 electron configuration present the same stereochemistry as that of the corresponding Ni(III) analogues, which has the low-spin d^7 configuration, and contains one unpaired electron (S = 1/2). The stability of Ni(III) compounds and the ESR measurements were studied previously [8] and were presented together with UV-Vis spectroscopy of tetraazamacrocyclic complexes.

In this paper we consider mainly the Ni(III) complexes, $[Ni^{III}LCl_2]^+$, containing tetraaza macrocyclic ligands with different number of methyl groups (L = [14]aneN$_4$ (L^1), 2-Me[14]aneN$_4$ (L^2), 5,12-Me$_2$[14]aneN$_4$ (L^3), 5,7,7,12,14,14-Me$_6$[14]aneN$_4$ (L^4)) obtained from the corresponding nickel(II) complexes by oxidation with hydrogen peroxide. The important part of our work consists of kinetic investigations of the one-electron oxidation process of $[Ni^{II}LCl_2]$ to $[Ni^{III}LCl_2]X$ with hydrogen peroxide in HCl-water solutions. The EPR and IR spectra as well as magnetic measurements confirm the suggested electronic structure of the complexes.

EXPERIMENTAL

Synthesis of nickel(II) complexes: The Ni(II) compounds were synthesized according to the procedure of [8]. Macrocyclic tetraamine nickel(II) complexes have been prepared by mixing equimolar amounts of $NiCl_2 \cdot 6H_2O$ or $Ni(ClO_4) \cdot 6H_2O$ and appropriate ligand in methanol. Perchlorate and trichloride salts were crystallized from methanol or methanol-acetone solutions. Cyclam (L^1) [9], meso-5,12-dimethylcyclams (L^3) [10], meso-5,7,7,12,14,14-hexamethylcyclam (L^4) [11] have been prepared according to known procedures. 2-Methylcyclam (L^2) was obtained by analogy to known cyclam [9] synthesis with 2-methylglyoxal instead of glyoxal [12]. Hydrochloric acid, perchloric acid, 30% hydrogen peroxide and solvents were commercial materials and were used without further purification.

Synthesis of 1,4,8,11-tetraazacyclotetradecanenickel(III)trichloride [Ni [14]aneN_4Cl_2]Cl: 1 g of tetraazacyclotetradecanenickel(II)trichloride was dissolved in 25 cm^3 of methanol containing 2 cm^3 of concentrated hydrochloric acid. After addition of 2 cm^3 of 30% hydrogen peroxide the mixture was stirred for 1 hour at room temperature. Precipitated yellow crystalline product was filtered off, washed with methanol and dried under reduced pressure. The compound was crystallized from methanol-acetone solution (yield 90–95%).

Brown [Ni [14]aneN_4Cl_2]Cl upon crystallization from 1M HCl gave green crystals of Ni [14]ane$N_4Cl_3 \cdot 5H_2O$.

Synthesis of [Ni meso-5,12-Me_2[14]aneN_4Cl_2]Cl·CH_3OH and [Ni meso-5,7,7,12,14,14-Me_6[14]aneN_4Cl_2]Cl: These compounds were obtained following the same procedure mentioned before and crystallized from methanol-acetone solution. Yield: 90–95%.

The second complex [Ni meso-5,7,7,12,14,14-Me_6[14]aneN_4Cl_2]Cl was very difficult to obtain and it contains about 8.5% of non-oxidized form because of superiority of planar structure in the initial Ni(II) complex. It was impossible to obtain a product with a higher purity level.

Synthesis of [Ni 2-Me[14]aneN_4Cl_2]ClO_4: The compound was obtained by H_2O_2/HCl oxidation of appropriate Ni(II) dichlorideperchlorates according to the same procedure and crystallized from methanol solution. Yield: 90%.

Analyses confirmed the compositions given.

Caution!: Though no danger was encountered in this experiment, perchlorate salts containing organic ligands should be prepared in small amounts and handled with care.

Kinetic measurements: Kinetics of oxidation of $Ni^{II}L^1Cl_2$, $Ni^{II}L^2Cl_2$ and $Ni^{II}L^3Cl_2$ with hydrogen peroxide have been investigated spectrophotometrically in water-HCl solutions under pseudo-first order conditions with the oxidant concentration in excess over the Ni(II) complexes. Oxidation reaction of $Ni^{II}L^4Cl_2$ with hydrogen peroxide in the same conditions was very slow and no changes in the absorbance have been observed over a period of several days. The stock solutions of nickel(II) complexes were freshly prepared before each series of measurements. Analytical reagent grade chemicals were used without further purification. The ionic strength was kept constant by adding NaCl from 1 mol dm^{-3} stock solution.

Electronic absorption spectra, as well as kinetic measurements were made on Specord UV-Vis spectrophotometer. Reaction rates were monitored at the absorbance maximum of Ni(III) complexes (λ = 312 nm) and the observed first order rate constants, $k_{obs.}$, were calculated by linear least-squares fitting of $\ln(A_\infty - A_t)$ to t. A_t and A_∞ are the absorbances of the solution at time t and after 8–10 half-lives, respectively. Each kinetic run was repeated 2–4 times.

Magnetic measurements: Magnetic susceptibility of a polycrystalline sample was measured by the Faraday method between 4.2–300 K, using a sensitive Sartorius M-25D electrobalance. The susceptometer was equipped with an Oxford Instruments CF-1200 continuous-flow cryostat and an electromagnet operating at 5 kG. Helium gas pressure of 10 Torr served as heat exchanger between the sample and the cold tube of the cryostat. The temperature was measured by means of goldiron (0.07 atomic%)-Chromel-P-thermocouple. The temperature of the reference junction was 77.4 K. The Faraday balance was calibrated with palladium powder sample, with a measured purity 99.9985% (Johnson Mathey Company, England). Magnetic susceptibility of compounds was corrected for diamagnetism of the constituent atoms, which was calculated using Pascal's constant [13] and the temperature-independent paramagnetism of Ni(III) ion ($N_\alpha = +250 \cdot 10^{-6}$ cm^3 mol^{-1}).

Spectroscopy: IR spectra (paraffin oil mulls) were recorded on a Perkin Elmer 1600 FTIR spectrometer. Solid state EPR spectra were recorded in the 300–77 K temperature range on a Bruker E600 spectrometer. Reflectance spectra have been recorded on Beckmann UV 5240 spectrophotometer in the range 350–2500 nm.

RESULTS AND DISCUSSION

Reaction rate measurements of oxidation of macrocyclic Ni(II) complexes with hydrogen peroxide in water-HCl solution in a broad range of reagents concentrations, pH and ionic strengths revealed first order kinetics with respect to the Ni(II) complexes. At the Ni(II) complexes in the range (1–20)$\times 10^{-5}$ mol dm^{-3} with hydrogen peroxide in 40–700 fold excess over the Ni(II) complexes, the pseudo-first order rate constant $k_{obs.}$ was proportional to the hydrogen peroxide concentration and reactions were exactly second order (Table 1). Studies in the range [HCl] = 0.02–0.5 mol dm^{-3} and ionic strength (I = 0.1 and 0.5 mol dm^{-3}) indicated zero order dependence in [H$^+$].

The following reaction mechanism with k_a as the rate determining step is consistent with the stoichiometry and kinetic results:

$$[NiL^n]^{2+} + H_2O_2 \xrightarrow{k_a} [NiL^n]^{3+} + HO + OH^-$$

$$[NiL^n]^{2+} + HO \xrightarrow{fast} [NiL^n]^{3+} + OH^-$$

This reaction mechanism leads to the rate law:

$$\frac{d[[NiL^n]^{3+}]}{dt} = 2k_a\,[[NiL^n]^{2+}][H_2O_2]$$

where $2k_a = k_{exp}/[H_2O_2] = k$. Axially coordinated ligands in nickel complexes are omitted for simplicity. It has been observed that Ni(III) complexes with nitrogen macrocyclic ligands are generally stable for long periods only in aprotic solvents [14]. Kinetic studies involving Ni(III) in aqueous media have so far been concerned primarily with the formation and decay of the trivalent state [15–17]. Axial coordination of simple ligands stabilizes Ni(III) complexes dramatically [1,8, 18–21]. The sequence of the stability constant for axial coordination of simple inorganic anions found by Zeigerson and co-workers [18] ($SO_4^{2-} \geq HPO_4^{2-} > H_2PO_4^-, Cl^- >> ClO_4^-$) is in agreement with the basicity of these ligands.

In the octahedral low-spin Ni(III) species two water molecules should occupy the axial sites, whereas the Ni(II) complex exists as an equilibrium mixture of the low-spin square form and the high-spin, diaqua octahedral form. Oxidation of the in-

Table 1. Observed first-order rate constants, $k_{obs.}$, for oxidation reactions of NiL^1Cl_2, NiL^2Cl_2 and NiL^3Cl_2 with hydrogen peroxide in 0.1 mol dm^{-3} HCl solution at 295 K, and derived second-order rate constants, k, at ionic strength $I = 0.1$ and 0.5 mol dm^{-3}.

10^5 [NiL^1Cl_2] (mol dm^{-3})	10^3 [H_2O_2] (mol dm^{-3})	10^2 $k_{obs.}$ (s^{-1})	10^5 [NiL^2Cl_2] (mol dm^{-3})	10^3 [H_2O_2] (mol dm^{-3})	10^2 $k_{obs.}$ (s^{-1})	10^5 [NiL^3Cl_2] (mol dm^{-3})	10^3 [H_2O_2] (mol dm^{-3})	10^2 $k_{obs.}$ (s^{-1})
4.02	9.20	2.17 ± 0.13	1.29	8.85	1.36 ± 0.04	2.59	9.82	0.67 ± 0.02
8.91	9.20	2.38 ± 0.12	3.83	8.85	1.51 ± 0.06	5.82	9.82	0.72 ± 0.03
18.1	9.20	2.14 ± 0.15	6.30	8.85	1.49 ± 0.05	19.3	9.82	0.63 ± 0.02
8.91	1.84	0.41 ± 0.02	3.83	1.77	0.32 ± 0.02	3.95	1.96	0.114 ± 0.006
8.91	3.68	0.95 ± 0.04	3.83	3.54	1.69 ± 0.10	3.95	3.93	0.244 ± 0.01
8.91	19.6	4.50 ± 0.22	3.83	17.7	2.79 ± 0.14	3.95	19.6	1.39 ± 0.07
k (mol^{-1} dm^3 s^{-1}) = 2.41 ± 0.13 at $I = 0.1$ and 3.40 ± 0.08 at $I = 0.5$			k (mol^{-1} dm^3 s^{-1}) = 1.69 ± 0.10 at I = 0.1 and 2.53 ± 0.07 at $I = 0.5$			k (mol^{-1} dm^3 s^{-1}) = 0.67 ± 0.05 at $I = 0.1$ and 1.03 ± 0.09 at $I = 0.5$		

Errors are the standard deviations. The values of second-order rate constants, k, were calculated from the rate measurements at pH = 1.0, 1.3 and 1.7 for the reactions at $I = 0.1$ mol dm^{-3}, and from the rate measurements at pH = 0.3 and 1.0 for the reactions at $I = 0.5$ mol dm^{-3}. Ionic strength was adjusted with NaCl. (For comparison, oxidation of $[NiL^1]^{2+}$ with hydrogen peroxide in 0.1 mol dm^{-3} sulphuric acid at 295 K is characterized by k equal to 0.19 mol^{-1} dm^3 s^{-1} [24]).

Table 2. Second order rate constant, k, at various temperatures, and thermodynamic parameters for oxidation of nickel(II) macrocyclic complexes with hydrogen peroxide in acidic water solution.

Complex	k (mol^{-1} dm^3 s^{-1})						$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
	281.2 K	282.7 K	295 K	298.2 K	308.2 K	309.2 K		
NiL^1Cl_2	1.08	1.33	2.4	3.7	6.2	7.4	45 ± 3	–84 ± 9
NiL^2Cl_2	0.53	0.68	1.75	1.90	4.2	4.0	49 ± 2	–73 ± 7
NiL^3Cl_2	0.20	0.21	0.66	0.83	1.46	1.75	53 ± 2	–68 ± 7

Reaction conditions: [H_2O_2] = 3.93 × 10^{-3} mol dm^{-3}, [HCl] = 0.1 mol dm^{-3}, [NiL^1Cl_2] = 8.31 × 10^{-5} mol dm^{-3}, [NiL^2Cl_2] = 4.65 × 10^{-5} mol dm^{-3}, [NiL^3Cl_2] = 4.12 × 10^{-5} mol dm^{-3}. Errors are the standard deviations.

vestigated complexes in the presence of the complexing, Cl^- anions, yields octahedral $[Ni^{III}LCl_2]^+$ species as reaction products [20]. The increase of NaCl concentration (Table 1) indicates the increase of the reactions rate, however in the presence of $NaClO_4$ the oxidation of Ni(II) to Ni(III) with hydrogen peroxide is considerably limited. In perchlorate media, there is evidence [20] for a rapid dissociation of one chloride ligand, and $[Ni^{III}(cyclam)Cl_2]^+$ species are present only in solutions with Cl^- concentration above 0.5 mol dm^{-3}. A similar effect has been noted by Meyerstein and co-workers [22] with $[Ni^{III}Me_6[14]aneSO_4]^+$, where coordination by an anion appears to impart the increased thermodynamic and kinetic stability.

The inhibition of the oxidation processes in the presence of perchlorate ions can be connected with the conversion of the more reactive high-spin octahedral form of Ni(II) to the low-spin square form. The investigations made by Fabrizzi and co-workers [23,24] carried in the $NaClO_4$ concentration range at 0.1–7 mol dm^{-3} showed that $[Ni^{II}(cyclam)]^{2+}$ takes the low-spin square form at $[ClO_4^-] > 3$ mol dm^{-3}. Besides, in the presence of perchlorate anions oxidative dehydrogenation of the ligand and subsequent coupling during the oxidation process of $[Ni^{II}(cyclam)]^{2+}$ with hydrogen peroxide yield binucleating nickel(II) macrocycles, where each nickel(II) ion is square planar [25].

Differences in the rate observed in the reactions of cyclam complexes compared to methylated macrocycles (Table 1) results from differences in the reduction potentials and steric hindrance for interactions with oxidant created by methyl substituents in the macrocyclic backbone. Presence of six methyl groups in macrocyclic ligand stops the oxidation of $[Ni^{II}L^4Cl_2]$ with hydrogen peroxide in water solutions. The process of oxidation of Ni(II) to Ni(III) goes distinctly easier in alcohol solutions, but even using 30% H_2O_2 the oxidation presents a limited yield.

The temperature dependences of the second-order rate constants, k, are presented in Table 2. The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated from linear plots of log (k/T) *vs.* (1/T) using Eyring transition-state theory.

Magnetic susceptibility measurements of three complexes investigated $[Ni[14]aneN_4Cl_2]Cl$, $[Ni\ 2\text{-}Me[14]aneN_4Cl_2]ClO_4$ and $[Ni\ meso\text{-}5,12\text{-}Me_2[14]aneN_4Cl_2]Cl \cdot CH_3OH$ reveal analogies in their magnetic properties. The average gram susceptibility χ_g and magnetic moment are shown in Table 3. All investigated complexes obey the Curie-Weiss law $\chi_M = C/(T - \Theta)$ between 100–300 K. The values of C and Θ are shown in Table 3. The magnetic moment shows stable values in the temperature range 30–300 K. There is a slight decrease of magnetic moment observed below the 30 K. The paramagnetic dependences of magnetic moment as a function of temperature are presented in Figs 1–4. Relatively lower value of μ_{eff} in $[Ni\ meso\text{-}5,7,7,12,14,14\text{-}Me_6[14]aneN_4Cl_2]Cl$ can be related to the impurity of Ni(II) form of the complex.

The EPR spectra show considerably greater values of $g_\perp$ than $g_\parallel$ for $[Ni\ meso\text{-}5,12\text{-}Me_2[14]aneN_4Cl_2]Cl \cdot CH_3OH$ and $[Ni\ meso\text{-}5,7,7,12,14,14\text{-}Me_6[14]aneN_4Cl_2]Cl$ complexes, as expected for a low-spin, d^7 metal centre in an elongated octahedral environment. Compounds $[Ni\ [14]aneN_4Cl_2]Cl$ and $[Ni\ 2\text{-}Me[14]aneN_4Cl_2]ClO_4$ give a

Table 3. The magnetic parameters of the investigated compounds – $^{*)}$ at room temperature and $^{**)}$ in the temperature range 50–300 K.

Compound	$\chi_g{*} \times 10^6$ (cm^3 g^{-1})	$\mu_{\text{eff.}}$*	Diamagnetic corrections $\times 10^6$ (cm^3 mol^{-1})	Mol$_{\text{wt.}}$	Weiss ** constant Θ (K)	Curie ** constant C (cm^3 K mol^{-1})
[Ni [14]aneN$_4$Cl$_2$]Cl	3.17	1.82	–236	365.4	1.92	0.409
[Ni 2-Me[14]aneN$_4$Cl$_2$]ClO$_4$	2.55	1.80	–256	443	1.55	0.406
[Ni meso-5,12-Me$_2$[14]aneN$_4$Cl$_2$]Cl·CH$_3$OH	2.65	1.83	–282	425.5	2.75	0.412
[Ni meso-5,7,7,12,14,14-Me$_6$[14]aneN$_4$Cl$_2$]Cl	2.31	1.54	–307	401.8	5.92	0.293

Table 4. EPR, IR and reflectance data of investigated compounds at room temperature and at 77 K in the brackets.

Compound	Spectroscopic splitting parameter			Reflectance spectra in solid state [band position (cm^{-1})]	IR spectra $\nu_{\text{N–H}}$ $\nu_{\text{O–H}}$ [cm^{-1}]
	g$_1$	g$_2$	g$_3$		
[Ni [14]aneN$_4$Cl$_2$]Cl	2.024 (2.056)	2.105 (2.098)	2.179 (2.183)	28600 12660	3137
[Ni 2-Me[14]aneN$_4$Cl$_2$]ClO$_4$	2.076 (2.079)	2.133 (2.158)	2.180 (2.181)	28570 12420	3198 3133
[Ni meso-5,12-Me$_2$[14]aneN$_4$Cl$_2$]Cl·CH$_3$OH	$g_{\|\|} = 2.026$ $(g_{\|} = 2.025)$		$g_\perp = 2.182$ $(g_\perp = 2.192)$	28570 12310	3144 3046 3541
[Ni meso-5,7,7,12,14,14-Me$_6$[14]aneN$_4$Cl$_2$]Cl	$g_{\|\|} = 2.027$ $(g_{\|\|} = 2.027)$		$g_\perp = 2.209$ $(g_\perp = 2.200)$	28570 12300	3168 3143

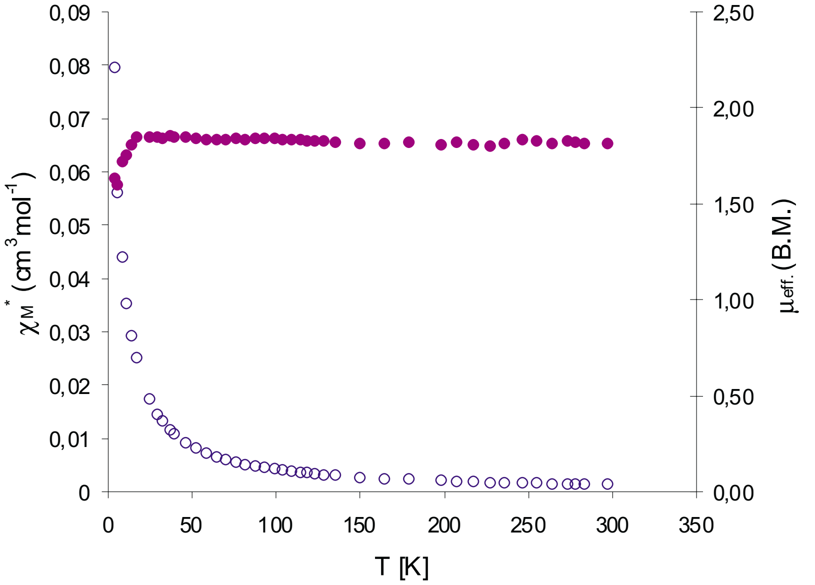

Figure 1. Experimental magnetic data of [Ni [14]aneN$_4$Cl$_2$]Cl plotted as a molar magnetic susceptibility χ_M (o) and magnetic moment $\mu_{\text{eff.}}$ (•) *vs*. temperature (Faraday data).

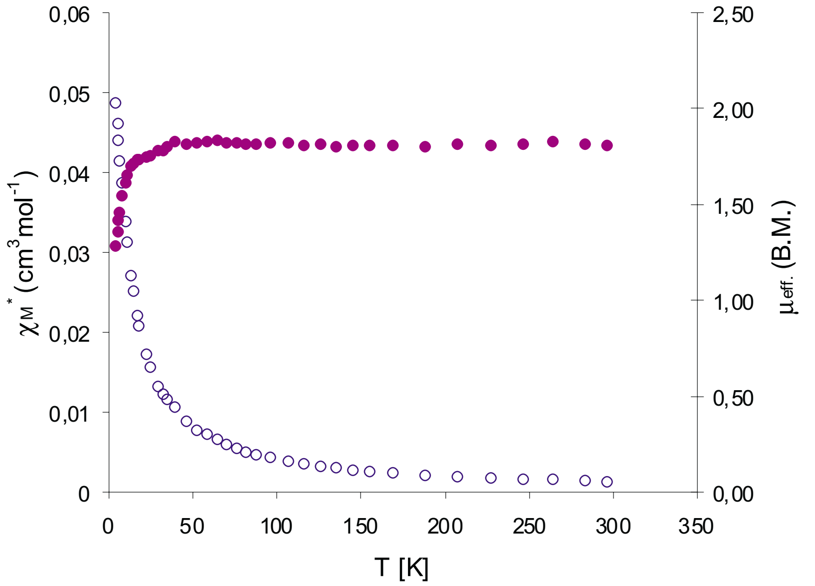

Figure 2. Experimental magnetic data of [Ni 2-Me[14]aneN$_4$Cl$_2$]ClO$_4$ plotted as a molar magnetic susceptibility χ_M (o) and magnetic moment $\mu_{\text{eff.}}$ (•) *vs*. temperature (Faraday data).

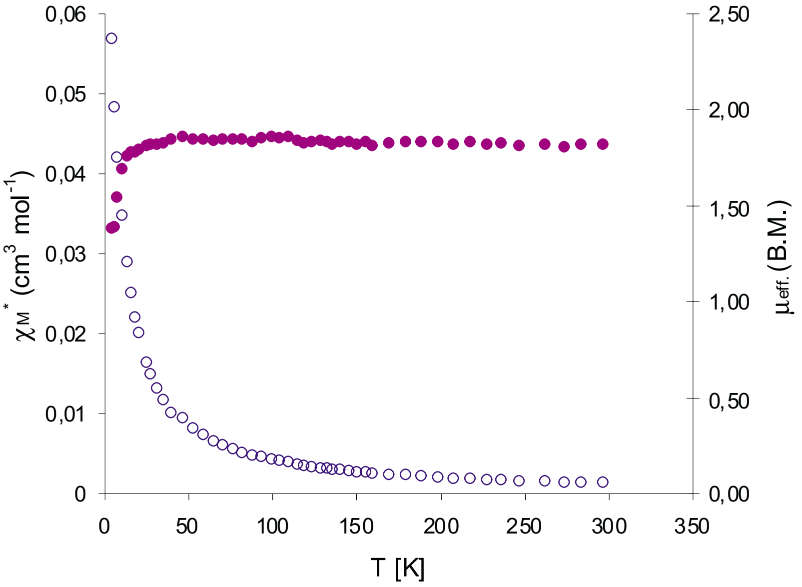

Figure 3. Experimental magnetic data of [Ni meso-5,12-Me_2[14]aneN_4Cl_2]Cl·CH_3OH plotted as a molar magnetic susceptibility χ_M (o) and magnetic moment $\mu_{eff.}$ (•) *vs.* temperature (Faraday data).

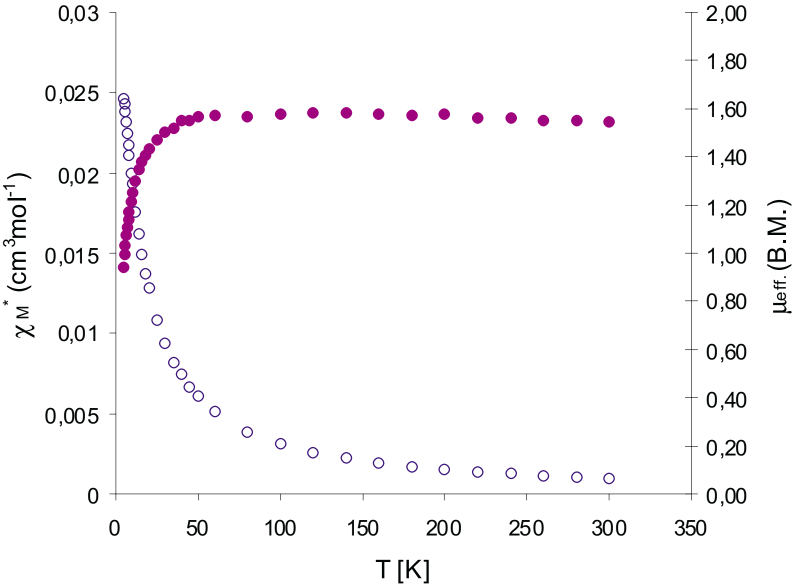

Figure 4. Experimental magnetic data of [Ni meso-5,7,7,12,14,14-Me_6[14]aneN_4Cl_2]Cl plotted as a molar magnetic susceptibility χ_M (o) and magnetic moment $\mu_{eff.}$ (•) *vs.* temperature (Faraday data).

rhombic EPR spectrum with g_1, g_2 and g_3 values presented in Table 4. If the first value is taken as a $g_{||}$ and the average of two values g_2 and g_3 is taken as pseudo- $g_{\perp}$, these two complexes belong (as well as the previous ones) to the class having $g_{\perp} > g_{||}$. The form of the EPR spectra for the low-spin Ni(III) complexes with $g_{\perp} > g_{||}$ suggests that the d_{z^2} orbital is favoured for the one unpaired electron. All the compounds investigated have very similar values of $g_{\perp}$ (as well as $g_{||}$) components. There is a slight increase of $g_{\perp}$ values observed, when the number of methyl groups in the molecule is increasing.

The solid-state reflectance spectra of these complexes consist of two bands at about 28600 and 12300 cm^{-1}. The position of the second band shifts to the lower frequency, while the number of the methyl groups in the complex is increasing. The EPR and reflectance data are presented in Table 4.

The IR spectra of all complexes show absorption of NH groups (ν_{NH}) between 3198 and 3046 cm^{-1}. One compound of formula [Ni meso-5,12-Me_2[14]aneN_4Cl_2]Cl exhibits a band at 3541 cm^{-1} originating from ν_{OH} of coordinated methanol presence. The positions of characteristic peaks in the IR spectra are presented in Table 4.

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