Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 363–367

Ni(II) COMPLEXES WITH LIGANDS RESULTED IN CONDENSATION OF N,N-DIMETHYLBIGUANIDE AND PENTANE-2,4-DIONE

Synthesis, thermal behaviour and spectroscopic characterization

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This paper deals with the first investigation concerning the thermal behaviour of Ni(II) complexes with ligands having biguanide moieties. The new complex $[NiL(1)](ClO_4)_2{\cdot}2.5H_2O$ (**1**) with the Schiff base resulted in [2+1] condensation of N,N-dimethylbiguanide with pentane-2,4-dione (L(1)) and the complex $[Ni_2L(2)](ClO_4)_4$ (**2**), with the Schiff base, L(2), resulted through the oxidative condensation of L(1) have been synthesized and characterised. The bonding and stereochemistry of the complexes have been characterized by IR and electronic spectra. The cyclic voltammograms show the characteristic waves for mononuclear and respectively binuclear Ni(II) complexes and indicate that both complexes exhibit catalytic effects on the CO_2 electrochemical reduction. The thermal behaviour provided confirmation of the complexes composition as well as the number and the nature of water molecules and the intervals of thermal stability. The different nature of the ligands generates a different thermal behaviour for complexes.

Keywords: *biguanide moiety, carbon dioxide, electrochemical reduction, template, thermal stability*

Introduction

There is much interest in synthesis and characterisation of nickel complexes with nitrogen donors ligands with particular attention focused on species that could present a similar behaviour with those of the natural nickel containing species. One of the natural occurring species F_{430}, a Ni(II) hydrocorphinoid complex, is a prosthetic group of S-methyl coenzyme M reductase which catalyzes the reductive cleavage of S-methyl coenzyme M to coenzyme M and methane in the final stage of carbon dioxide reduction in the methanogenic bacteria [1]. The design and synthesis of electrocatalyses that could perform the reduction of the CO_2 may be important in lessening of the greenhouse effect and in developing new energetic source. The reduction process involve two-, four-, six- or eight-electron as a function of the reaction products that could be CO, formic acid, formaldehyde, methanol or methane. The high activation energy of CO_2 reduction at the platinum electrode requires a more negative potential than –2.24 V *vs*. SCE but this can be lowered by using catalysts. So far, the catalytic effects on the electrochemical reduction of CO_2 were evidenced for some transition metal complexes [2–4]. Some of these, are mono-, di- or trinuclear Ni(II) complexes with macrocyclic ligands [5–9]. It was shown that these compounds perform the electrochemical reduction of CO_2 to CO or formate anion by shifting the CO_2 reduction potential by ca. 0.5 V. Moreover, in order to obtain the reduction products involving more than two electrons; polynuclear complexes should be employed [9]. Such type of compounds also presents a high thermodynamic and kinetic stability and there are no studies concerning its thermal behaviour. On the basis of these considerations we have been synthesised complexes of Ni(II) with ligands resulted by template condensation of pentane-2,4-dione and N,N-dimethylbiguanide and respectively by oxidative condensation of the ligand resulted in this process. The complexes were formulated on the basis of analytical and spectral data. The redox behavior of these complexes in argon and respectively carbon dioxide indicate that both complexes can catalyze the electroreduction of carbon dioxide. The thermal decomposition of these complexes was used in order to confirm the composition and also in order to obtain information about the interval of the thermal stability of these species.

Experimental

All reagents were of commercial analytical quality and have been used without further purification. Chemical analysis of carbon, nitrogen, sulphur and hydrogen has been performed using an EA 1110 analyzer. Nickel was determined gravimetrically using dimethylglyoxyme in the laboratories of Inorganic Chemistry Department.

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1388–6150/$20.00

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IR spectra were recorded in KBr pellets with a Bio-Rad FTIR 135 spectrometer in the range 400–4000 cm^{-1}. Electronic spectra by diffuse reflectance technique, with MgO as standard, were recorded in the range 380–1100 nm, on a VSU 2P-Zeiss Jena spectrometer. The voltammetric measurements were accomplished with a polarographic and voltammetric ensemble Trace Master 5 and POL 150 Polatrographic Analyzer (Radiometer Copenhapen). Cyclic voltammetry was carried out in DMF/H_2O (1:9, *v*/*v*) containing 0.1 M $NaClO_4$. The working electrode was HMDE (hanging mercury drop electrode), the auxiliary electrode was a coiled platinum wire, and the reference electrode was Ag/AgCl. The dissolved oxygen from the analyzed solution was eliminated by bubble a pure argon stream.

The heating curves (TG, T, DTA and DTG) were recorded in a static air atmosphere using a Shimadzu DTG-TA-51H thermogravimetric analyzer with a sample mass of 15 and 6 mg over the temperature range 20–1000°C, using a heating rate of 10 K min^{-1}.

Synthesis of the complexes

Compound $[NiL(1)](CH_3COO)_2\cdot2.5H_2O$ (**1**)

To a solution of nickel(II) acetate (5 mmol, 1.244 g), dimethylbiguanide chlorhydrate (10 mmol, 1.655 g) in 100 mL ethanol was added dropwise (5 mmol, 0.51 mL (d=0.975 g mL^{-1})) pentane-2,4-dione. The reaction mixture was refluxed 48 h until an orange compound was formed. The microcrystalline product was filtered off, washed with EtOH, Et_2O and air-dried. Analysis, found: Ni, 10.68; C, 37.48; H, 6.88; N, 25.78%; $NiC_{17}H_{37}N_{10}O_{6.5}$ requires: Ni, 10.79; C, 37.52; H, 6.85; N, 25.74%; IR (KBr pellet), cm^{-1}: ν(OH), 3430m, sh; ν(NH), 3369s, 3304m, 3262m; $\nu_{as}(CH_3)$, 2930m; $\nu_s(CH_3)$, 2840m; ν(C=N), 1683vs; ν_{as}(COO), 1640vs; $\delta(NH_2)$, 1519m; ν_s(COO), 1436m; ν(Ni–N), 475w.

Compound $[Ni_2L(2)](CH_3COO)_4$ (**2**)

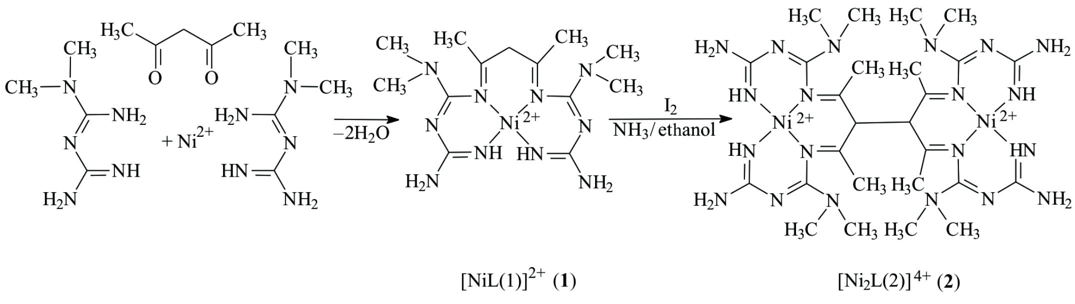
To a suspension of $[NiL(1)](CH_3COO)_2\cdot2.5H_2O$ (2 mmol, 1.088 g) in 50 mL ethanol was added an aqueous concentrated ammonia solution (5 mL) and iodine (1 g). The reaction mixture was magnetically stirred at 50°C for 4 h until a deep orange compound was formed. The microcrystalline product was filtered off, washed with ethanol, ether and air-dried. Analysis, found: Ni, 11.71; C, 40.82; H, 6.38; N, 28.18%; $Ni_2C_{34}H_{62}N_{20}O_8$ requires: Ni, 11.78; C, 40.98; H, 6.27; N, 28.11%; IR (KBr pellet), cm^{-1}: ν(NH), 3367s, 3269s, 3160s; $\nu_{as}(CH_3)$, 2950m; $\nu_s(CH_3)$, 2830m; ν(C=N), 1687vs; ν_{as}(COO), 1648vs; $\delta(NH_2)$, 1514m; ν_s(COO), 1428m; ν(Ni–N), 424w.

Results and discussion

Synthesis and physico-chemical characterisation of the complexes

The template condensation reaction of polyamines with polycarbonyl derivatives is the subject of many studies. Using this method there were synthesised a great number of macrocyclic compounds containing azomethynic groups [10]. We have synthesised ligands containing biguanide residues by condensation of N,N-dimethylbiguanide (DMBG) and pentane-2,4-dione (Scheme 1). The synthesis has been performed in order to obtain azamacrocyclic complexes bearing biguanide moieties as part of the ligand superstructure. However it is to be mentioned that no matter of the molar ratio between the organic components, the final ligand is acyclic and it corresponds to a [2+1] condensation of N,N-dimethylbiguanide and pentane-2,4-dione. Considering that the molecular mechanics simulation of N,N-dimethylbiguanide indicate that the lower charge density appear on the N^2 we have been considered that this group is the most susceptible of the nucleophilic attack of the carbonyl groups of acetylacetone.

The oxidative condensation of complex (**1**) in excess iodine in an alkaline medium produced the species $[Ni_2L(2)](ClO_4)_4$ (**2**) as it is shown in Scheme 1. This method was successfully performed on the S-alkylisothiosemicarbazide derivatives [11] that suffer the condensation process not only in the presence of iodine but also with oxygen. Our study has evidenced that the



Scheme 1

biguanide derivatives suffer the oxidative condensation only in the presence of the iodine.

The two complexes are polycrystalline solids soluble in N,N-dimethylformamide while the complex (**2**) is water soluble too.

The major IR spectral features of complexes presented at experimental part indicate that in the spectra of complexes appear the characteristic bands of biguanide moieties [12]. The bands corresponding to NH and C=N vibration modes are significantly shifted toward higher wavenumbers in the spectra of the complexes. This behaviour could arise from the breaking of the hydrogen bonds network, from the condensation process and also from the coordination. At 1345 cm^{-1} appears for both complexes a new band. This band was observed in the spectra of some complexes with biguanide derivatives [12, 13] and can be associated either with the formation of the chelate ring or with the activation of an IR band as a result of the ligand symmetry decrease upon coordination. In the range characteristic for the carboxylic vibrations, the spectra of the complexes display two bands. The position of these bands is in accord with the presence of the free acetate [14]. The spectrum of complex (**1**) in the characteristic ranges for water shows a shoulder about 3430 cm^{-1} assigned to ν(OH) stretching vibrations [15].

The diffuse-reflectance spectrum of complex (**2**) (Fig. 1) is characteristic for Ni(II) complexes with square-planar stereochemistry showing a narrow and symmetrical band centred at 470 nm. In the spectrum of complex (**1**) it can be seen one broad band, as it is usually observed for Ni(II) complexes with ligands that generate a strong field and moreover are dissymmetric [16].

The absence of the symmetry centre of the complexes allows the appearance of the three components, very closely as energy, that generates the broad aspect of the spectra. The absorption at 395, 505 and 610 nm could be assigned to the spin allowed transition $^1A_1 \rightarrow {}^1A_2$, $^1A_1 \rightarrow {}^1E$, $^1A_1 \rightarrow {}^1B_1$.

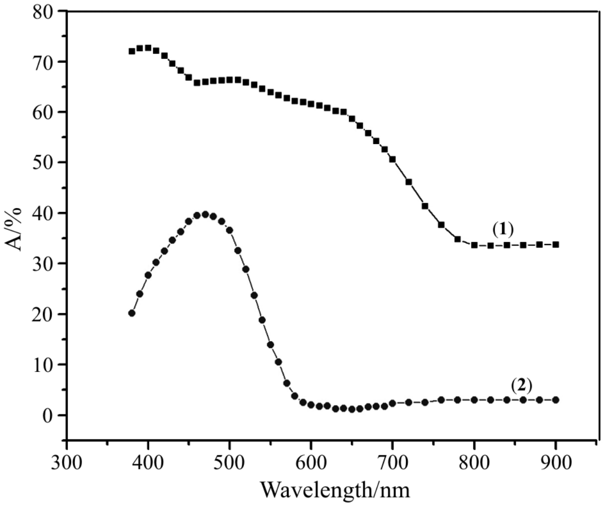


Fig. 1 Electronic spectra of complexes (**1**) and (**2**)

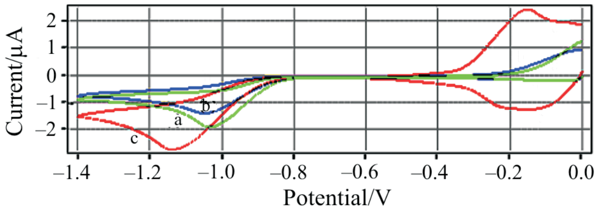


Fig. 2 Cyclic voltammogram of a – $[Ni(DMBG)_2](CH_3COO)_2$, b – complex (**1**) and c – (**2**) at a platinum electrode in DMF/H_2O (1:9, *v*/*v*) measured under argon (HMDE, working electrode; concentration of complex, 10^{-4} M; electrolyte, 0.1 M $NaClO_4$; scan rate, 200 mV s^{-1})

The cyclic voltammogram of complex (**1**) under argon atmosphere (Fig. 2) shows a cathodic peak at $E_{1/2}=-1.046$ V *vs.* Ag/AgCl corresponding to a unielectronic reduction for Ni(II)/Ni(I) couple. The reduction peak for complex (**2**) ($E_{1/2}=-1.138$ V) is wider than corresponding to compound (**1**) indicates that the electrochemical process involved two electrons in this case. As it is shown in Fig. 2 the two cyclic voltammograms are different one from the other and it is also different comparing with the one presented by $[Ni(DMBG)_2](CH_3COO)_2$ indicating that the processes of condensation occurred. Thus the new obtained ligands generated bonds different as strength that results in different redox behaviour.

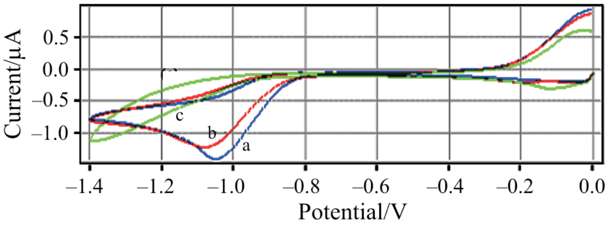


Fig. 3 Cyclic voltammogram of complex (**1**) at a platinum electrode in DMF/H_2O (1:9, *v*/*v*) measured a – under argon and b, c – under CO_2 (HMDE, working electrode; concentration of complex, $2\cdot10^{-4}$ M; electrolyte, 0.1 M $NaClO_4$; scan rate, 200 mV s^{-1})

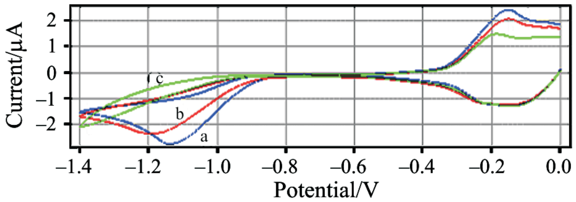


Fig. 4 Cyclic voltammogram of complex (**2**) at a platinum electrode in DMF/H_2O (1:9, *v*/*v*) measured a – under argon and b,c – under CO_2 (HMDE, working electrode; concentration of complex, $2\cdot10^{-4}$ M; electrolyte, 0.1 M $NaClO_4$; scan rate, 200 mV s^{-1})

The cyclic voltammograms recorded under CO_2 atmosphere indicate for both complexes the decrease of the current intensity and the shifting of the $E_{1/2}$ toward more negative potentials. When the solution was saturated with CO_2 the cathodic peak disappeared as it can be seen in Figs 3 and 4. This behaviour indicates that the complexes catalysed the CO_2 electrochemical reduction.

Thermal behaviour of the complexes

Thermal behaviour of complexes was investigated by thermogravimetry and the final residues were examined by X-ray diffraction on powder. The majority of intermediate products formed during thermal analysis were not possible to identify because the steps were not distinct. The excepts are the anhydrous complex formed after the first decomposition step of complex (**1**) and the intermediates formed at 350ºC for both complexes. Also, it was observed that the two complexes have a different thermal behaviour (Figs 5 and 6).

For complex (**1**) the water loss occurs in a single step, until 150°C (Table 1). This indicates the uncoordinated nature of the water molecules. The anhydrous species (square-planar, too) is very stable, its oxidative degradation begins at 240ºC. This step, exothermic one, results from at least two processes corresponding to acetate transformation into carbonate and to partial oxidative degradation of the ligand. In the next two steps the ligand suffers some oxidative transformations. The chemical composition of the intermediates cannot be determined due to multidirectional course of the Schiff base thermal degradation. Most probably, demethylation and deammination reactions occur (according to the mass loss). Such behaviour was also observed during the thermal transformation of other complexes with ligands having a complex structure [17] as well as for multifunctional organic derivatives [18].

The resulted species of these thermal transformation are Ni(II) complexes with paracyanide (having different polymerisation degree). The paracyanide formation was confirmed by the chemical analysis and IR spectra (ν(C=N) 1630 cm^{-1}) of intermediates.

For complex (**2**) the thermal behaviour is according to the proposed formulation for (**1**) on the basis of the chemical analysis, spectral data and voltammetric studies. This compound is even more stable than (**1**), the thermal decomposition starting at 257ºC. The first exothermic step corresponds to a partial oxidative degradation of the ligand in two processes (as TG indicates). The second one consists in transformation of acetate in carbonate according to the mass loss (Table 1). In the next step occurs the oxidative degradation of the residual ligand and the carbonate decomposition.

The last degradation steps lead to NiO as final product in the both cases, as XRD indicates.

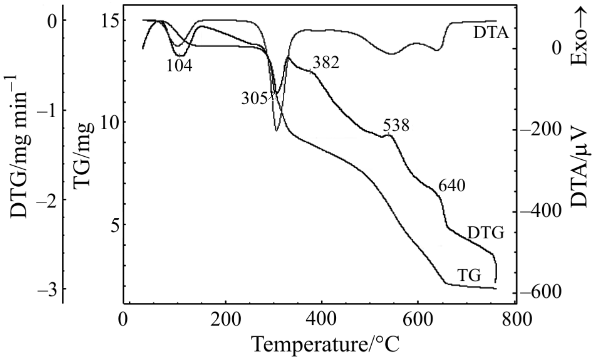


Fig. 5 The TG, DTG and DTA curves of (**1**)

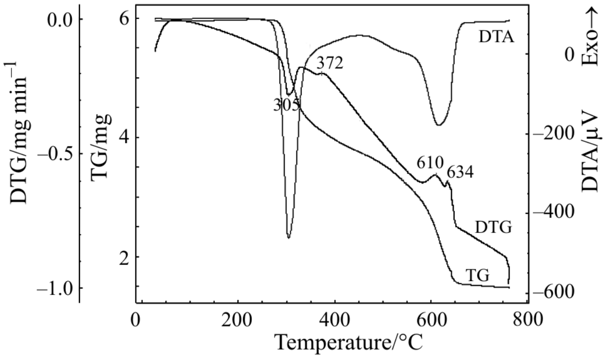


Fig. 6 The TG, DTG and DTA curves of (**2**)

Table 1 Thermal behaviour data (in static air atmosphere) for the complexes

Complex	Step	Thermal effect	Temperature interval/°C	Δm_{exp}/%	Δm_{calc}/%
$[NiL(1)](CH_3COO)_2\cdot 2.5H_2O$ (**1**)	1	endo	56–150	8.22	8.27
	2	exo	240–352	29.66	29.21
	3	exo	352–476	10.03	10.02
	4	exo	476–597	24.64	24.50
			597–706	13.36	13.23
			residue (NiO)	14.09	13.79
$[Ni_2L(2)](CH_3COO)_4$ (**2**)	1	endo	257–348	36.63	36.93
	2	exo	348–452	11.38	11.64
	3	exo	452–682	37.13	37.33
			residue (NiO)	14.86	14.10

Conclusions

The nickel(II) complexes with ligand resulted in [2+1] condensation of N,N-dimethylbiguanide and 2,4-pentanedione and respectively in their oxidative condensation have been synthesized.

The bond and stereochemistry were characterised by means of IR and electronic spectroscopy. According to the electronic spectra the proposed stereochemistry is square planar for both complexes.

The cyclic voltammograms are characteristic for mononuclear and binuclear Ni(II) complexes respectively and indicate that both complexes exhibit catalytic effects on the CO_2 electroreduction.

Thermal decomposition of complexes gave the possibility to establish the number and nature of water molecule, the composition of complexes and also the intervals of thermal stability. In order to confirm the nature of final residues and some intermediates the chemical analysis, IR spectra and X-ray diffractograms were performed.

References

1 R. P. Gulsalus and R. S. Wolfe, J. Bacteriol., 135 (1978) 851.
2 E. Kimura, M. Haruta, T. Koike, M. Shionoya, K. Takenouchi and Y. Itaka, Inorg. Chem., 32 (1993) 2779.
3 F. Abba, G. D. Santis, L. Fabbrizzi, M. Licchelli, A. M. M. Lanfredi, P. Pallavicini, A. Poggi and F. Ugozzoli, Inorg. Chem., 33 (1994) 1366.
4 R. W. Hay, J. A. Crayston, T. J. Cromie, P. Lightfoot and D. C. L. de Alwis, Polyhedron, 16 (1997) 3557.
5 M. Beley, J. P. Collin, R. Rupert and J. P. Sauvage, J. Chem Soc. Chem. Commun., (1984) 1315.
6 M. Beley, J. P. Collin, R. Rupert and J. P. Sauvage, J. Am. Chem Soc., 108 (1986) 7461.
7 J. P. Collin, A. Jouaiti and J. P. Sauvage, Inorg. Chem., 27 (1988) 1315.
8 E. Fujita, J. Haff, R. Sanzenbacher and H. Elias, Inorg. Chem., 33 (1994) 4627.
9 E. Y. Lee, D. Hong, H. W. Park and M. P. Suh, Eur. J. Inorg. Chem., (2003) 3242.
10 G. Foulds, Coord. Chem. Rev., 169 (1998) 3.
11 V. Arion, K. Wieghardt, T. Weyhermueller, E. Bill, V. Leovac and A. Rufinska, Inorg. Chem., 36 (1997) 661.
12 P. V. Babykutty, C. P. Prabhakaran, R. Anantaraman and C. G. R. Nair, J. Inorg. Nucl. Chem., 36 (1974) 3685.
13 G. Patrinoiu, L. Patron, O. Carp and N. Stanica, J. Therm. Anal. Cal., 72 (2003) 489.
14 G. B. Deacon and J. R. Philips, Coord. Chem. Rev., 33 (1980) 217.
15 K. Nakamoto, ‘Infrared and Raman Spectra of Inorganic and Coordination Compounds’, Wiley, New York 1986, p. 228.
16 A. B. P. Lever, ‘Inorganic Electronic Spectroscopy’, Elsevier, Amsterdam, London, New York 1986, p. 507.
17 F. C. D. Lemos, M. Muraro, J. Zukerman-Schpector, É. T. G. Cavalheiro and E. R. Dockal, J. Therm. Anal. Cal., 75 (2004) 599.
18 M. Wesolowski, E. Kosecka, J. Erecińska and K. Kobyłczyk, J. Therm. Anal. Cal., 74 (2003) 465.