Inorganica
Chimica Acta
LETTER

Thermally Dependent Structure of the Ni(II)–Hexacyclen Complex

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(Received August 7, 1989)

1,4,7,10,13,16-Hexaazaoctadecane (hexacyclen; Hex) proved to be an excellent complexation agent and extragent for different metal ions [1–9]. Our recent studies have proved that because of the flexibility of the ligand molecule, complexes with different geometrical structures are formed, some of them being temperature dependent [8, 9].

Ni(II)–hexacyclen complex formation has been already studied [1, 2] and, on the basis of electronic spectral data (d–d bands at 11980, 18850 and 28980 cm^{-1} [2]), an octahedral structure was assumed. Taking into account, however, the formation of temperature-dependent structures for Cu(Hex)·2TBP and Fe(Hex)·2TPB (TPB = tetraphenylborate) [8, 9], the aim of the present study was to perform EPR and magnetochemical investigation of Ni(Hex)·2TPB in the temperature range 100–370 K, in order to obtain more detailed structural information.

Experimental

The complex $Ni(Hex)^{2+}$ was synthesized from $NiCl_2·4H_2O$ (Merck) and hexacyclen·$3H_2SO_4$ (Aldrich), as described in the literature [2] and was precipitated with NaTPB (R. de Haen).

The magnetochemical measurements were performed in an argon atmosphere, according to the Faraday method. EPR spectra were taken on an ERS-220 X-band EPR spectrometer (GDR) in the range 100–370 K, as already described [7–9].

Results and Discussion

The magnetochemical measurements proved that Ni(Hex)·2TPB is paramagnetic with $\mu_{eff} = 2.8$ BM at ambient temperature. In Fig. 1 the temperature dependence of μ_{eff} of the complex is represented. These data indicate an octahedral symmetry ($\mu_{eff} \approx$ 2.8–3.1 BM) as the square-planar complexes are diamagnetic, and for the tetrahedral ones higher μ_{eff} values (3.2–4.0 BM) are expected [10]. The rather surprising fact should be noted that above 280 K the μ_{eff} values become lower and also the observed significant temperature dependence of μ_{eff} in the range 130–260 K.

Additional structural information was obtained by a study of the EPR spectra of the system at different temperatures. Typical EPR spectra are shown in Fig. 2. It should be noted that the increase and

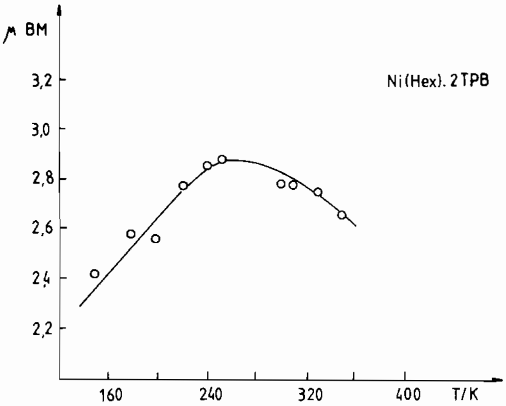

Fig. 1. Dependence of μ_{eff} with temperature for Ni(Hex)·2TPB.

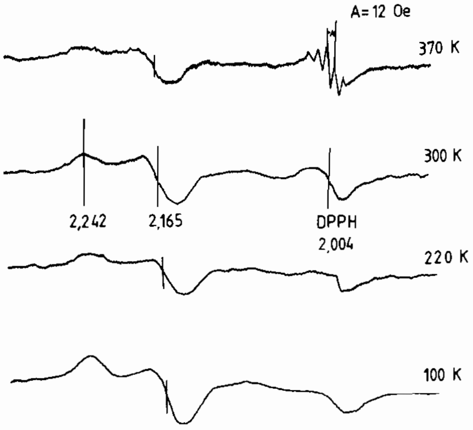

Fig. 2. EPR spectra of Ni(Hex)·2TPB at different temperatures.

decrease of the signal intensities and the high-frequency signal resolution of the g' signal are totally reversible, no hysteresis effects being observed.

It is evident that over the whole temperature range studied (100–370 K) two EPR signals are observed: a two-component anisotropic EPR signal ($g_\parallel = 2.242$, $g_\perp = 2.165$), the intensity of which decreases with temperature, and a singlet line ($g' = 2.004$) showing increasing intensity with temperature. It should be noted that at 370 K the latter shows resolved high-frequency signals of at least seven components ($A = 12$ Oe).

The unusual temperature dependence of μ_{eff} (Fig. 1) and the presence of two different signals in the EPR spectrum indicate the existence of two paramagnetic species. The anisotropic signal is typical of octahedral Ni(II) complexes [11], thus confirming the hypothesis of an octahedral structure for Ni(II)–Hex [2] at ambient temperature.

The presence of the EPR signal with $g' = 2.004$ might be attributed to a free radical formed as a result of reverse partial charge transfer from ligand to metal in the complex Ni(II)–Hex

$$\mathrm{Ni^{II}(Hex)} \rightleftharpoons \mathrm{Ni^{I}{-}R^{\bullet}} \qquad (1)$$

The formation of similar metal-stabilized ligand radicals ($g \approx 2.002–2.008$) of this type has already been proved, the latter resulting from reduction of Ni(II)–N_4-macrocyclic complexes [12, 13]. The formation of some Ni(I) species might not be observed in the EPR spectrum of the system, taking into account that its anisotropic signals ($g_\parallel \approx 2.22$ and $g_\perp \approx 2.006$ [12, 13]) overlap with the signals of Ni(II) and the stabilized radical, and the concentration of the latter should be relatively low.

The assumption that process (1) takes place in the system studied is also in agreement with the observed $\mu_{eff}–T$ dependence: the formation of Ni(I) species characterized with $\mu_{eff} \approx 1.85$ BM (d^9) should lead to a decrease in the μ_{eff} value.

The possibility of the stabilization of Ni(I) in the presence of hexacyclen was checked separately. For this purpose $\mathrm{Ni(Hex)^{2+}}$ was reduced with $NaBH_4$ (three-fold excess) in a H_2 atmosphere. In the course of the reduction the green colour of $\mathrm{Ni(Hex)^{2+}}$ changed to blue, and in the EPR spectrum of the frozen reaction mixture (77 K) a singlet isotropic line ($g = 2.029$) was observed, which might be assigned to the Ni(I) species.

Acknowledgement

This study was carried out as part of Contract 138/1988-89 sponsored by the Bulgarian Committee of Science.

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