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Visible Spectra of the Complex Species $Ni(en)_3^{2+}$, $Ni(en)_2(H_2O)_2^{2+}$ and $Ni(en)(H_2O)_4^{2+}$ from Kinetic Studies

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It has been shown by several authors [1–3] that acid hydrolysis of the complex cation $Ni(en)_3^{2+}$ (en = 1,2-diamino-ethane) is a three-step process which follows reaction (1):

$$Ni(en)_3^{2+} \xrightarrow{k_1} Ni(en)_2(H_2O)_2^{2+} \xrightarrow{k_2} Ni(en)(H_2O)_4^{2+} \xrightarrow{k_3} Ni(H_2O)_6^{2+} \quad (1)$$

At 25 °C the following rate data were obtained [1]:

$k_1 = 86.6\ s^{-1}$; $k_2 = 5.2\ s^{-1}$; $k_3 = 0.145\ s^{-1}$

Applying a rapid-scanning spectrometer Moore *et al.* [3] reported values of λ_{max} (wavelength of maximum absorption) and ϵ_{max} (absorption coefficient at λ_{max}) for the species $Ni(en)_2(H_2O)_2^{2+}$ and $Ni(en)(H_2O)_4^{2+}$. These data were taken from the spectra obtained at intermediate stages of the hydrolysis process.

The present contribution presents data for λ_{max} and ϵ_{max} of the above mentioned species which were obtained by studying reaction (1) with a newly designed, high resolution rapid-scan-stopped-flow spectrophotometer [4] and by analyzing a total of 90 spectra with a computer program producing time-independent values of λ_{max} and ϵ_{max} for the intermediates.

Experimental

In the stopped-flow experiment equal amounts of a 0.10 M $Ni(en)_3^{2+}$ solution (0.10 M in reagent grade $NiCl_2 \cdot 6H_2O$ and 0.355 M in freshly distilled 'en', which corresponds to 18% excess of the ligand) and of 1.0 M HCl were mixed.

The set-up and the specifications of the rapid-scan-stopped-flow spectrophotometer have been described elsewhere [4]. In the stopped-flow experiment a total of 90 spectra were taken in the wavelength range 304–725 nm. The absorbance/time data at 5 different wavelengths were fitted to function (2), which led to values for a_0, a_1, a_2, a_3 and

$$A = a_0 + a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t) \quad (2)$$

averaged values for k_1, k_2, k_3 by an iteration procedure. On the basis of the averaged rate constants the amplitudes a_i for all wavelengths (*i.e.*, the complete spectra) were calculated. The spectra of all four species involved in reaction (1) were finally calculated on the basis of the amplitudes a_i.

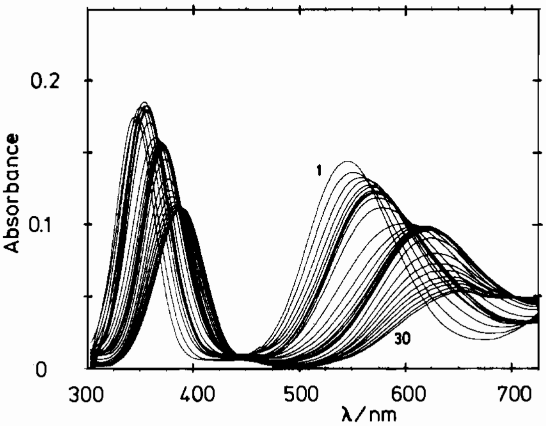

Fig. 1. Spectral changes observed for the various stages of reaction (1) at 5 °C with Δ*t* (time interval between 2 consecutive spectra) being 30 ms (spectra 1–10), 600 ms (spectra 11–20) and 15 s (spectra 21–30).

Results and Discussion

Figure 1 presents every third spectrum out of a total of 90 spectra taken in a typical stopped-flow experiment. The spectra were taken at three different time bases, Δ*t* (time interval between two consecutive spectra) being 10 ms in the beginning (spectra 1–29), 200 ms in the middle (spectra 30–59) and 5 s at the end (spectra 60–89). It is obvious that during the hydrolysis process the spectra are red-shifted, in both the wavelength range 350–400 nm ($^3T_1(P) \leftarrow {}^3A_2$) and 550–650 nm ($^3T_1(F) \leftarrow {}^3A_2$). This red-shift is accompanied by a loss in intensity for both absorption bands.

Computer fitting of the absorbance/time data to eqn. (2) at 5 different wavelengths leads to the rate constants listed in Table I. It follows that the rate of hydrolysis decreases with decreasing numbers of chelate ligands being coordinated, *i.e.*, k_1:k_2:k_3 = 533:30:1. The comparison with the rate constants reported in the literature [1, 3] suffers from the fact that the studies were carried out at different temperatures. Using the activation energies pre-

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TABLE I. Rate Constants for Reaction (1) at 5 °C

k_1 (s^{-1})	k_2 (s^{-1})	k_3 (s^{-1})	k_1/k_2	k_2/k_3	Reference
11.4 ± 1.0	0.645 ± 0.014	0.0214 ± 0.0011	17.7	30.1	this work
11	0.54	0.015	20.6	36.0	1[a]
6.8	0.28	0.013	24.3	21.5	3[a]

[a]Rate constants at 5 °C calculated from those at higher temperature with the activation energies given in ref. 1.

TABLE II. Wavelengths of Maximum Absorption (λ_{max}) and Absorption Coefficients (ϵ_{max}) of the Species Involved in Reaction (1)

Species	$^3T_1(P) \leftarrow {}^3A_2$		$^3T_1(F) \leftarrow {}^3A_2$		Reference
	λ_{max} (nm)	ϵ_{max} (nm)	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	
$Ni(en)_3^{2+}$	343.8 ± 1	7.7	542.8 ± 1	6.2	this work
	345 ± 5	7.8	550 ± 5	6.0	3
$Ni(en)_2(H_2O)_2^{2+}$	356.4 ± 1	7.9	570.1 ± 1	5.2	this work
	360 ± 5	7.8	570 ± 5	5.0	3
$Ni(en)(H_2O)_4^{2+}$	371.5 ± 1	6.6	620.5 ± 1	4.1	this work
	373 ± 5	6.7	625 ± 5	3.8	3
$Ni(H_2O)_6^{2+}$	388.3 ± 1	5.3	651.8 ± 1	1.9	this work
	390 ± 5	5.1	650 ± 5	1.6	3

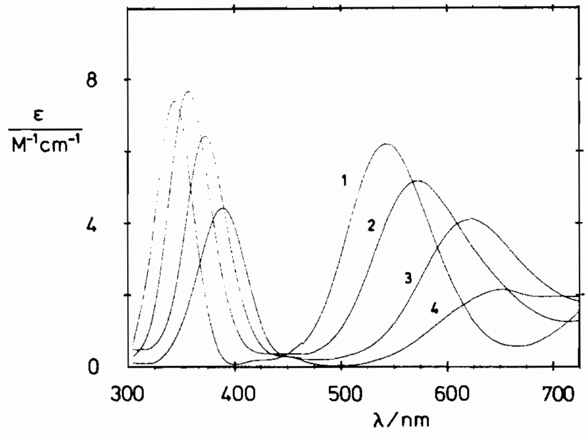

Fig. 2. Visible spectra of the species $Ni(en)_3^{2+}$ (1), $Ni(en)_2(H_2O)_2^{2+}$ (2), $Ni(en)(H_2O)_4^{2+}$ (3) and $Ni(H_2O)_6^{2+}$ (4) at 5 °C.

sented by Wilkins *et al.* [1] for converting all rate constants to 5 °C one obtains the data given in Table I. Considering the errors involved (the activation parameters have an error of more than 5%) the agreement is acceptable.

Computer approximation of the absorption coefficients ε of all four species involved in reaction (1) leads to the spectra shown in Fig. 2 and to the values of λ_{max} and ϵ_{max} listed in Table II. These values prove indeed the red-shift and the loss in intensity which accompanies the loss of coordinated chelate ligands, *i.e.*, the stepwise transition from the NiN_6 coordination to the NiO_6 coordination. Due to the fact that the resolution of the diode array spectrophotometer used in this work (0.8 nm/diode) is much better than that of the set-up used by Moore *et al.* [3] the error in λ_{max} is only ±1 nm. In addition, the way in which the spectra of the intermediates were calculated (see 'Experimental') excludes any contributions from other species. The agreement between the values for λ_{max} and ϵ_{max} obtained in this work and those obtained from intermediate spectra [3] is nevertheless sufficiently good.

The intermediate $Ni(en)_2(H_2O)_2^{2+}$ could possibly exist in the *cis* or *trans* forms. It follows from the experimental evidence presented by Moore *et al.* [3] that the observed spectrum of the species $Ni(en)_2(H_2O)_2^{2+}$ corresponds well with that of known *cis* octahedral species.

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