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FULL PAPER

Equilibrium and kinetic studies on the formation of mono- and bi-nuclear Ni^{II} complexes with a binucleating hexaaza macrocycle†

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The stability and kinetics of formation of Ni^{II} complexes with the macrocyclic ligand 3,6,9,17,20,23-hexaazatricyclo-[23.3.1.1^{11,15}]triaconta-1(29),11(30),12,14,25(26),27-hexaene (L) that contains two diethylenetriamine sub-units linked by *m*-xylyl spacers has been studied in water solution. The equilibrium studies indicate the formation of several mono- and bi-nuclear metal complexes. However, only mononuclear species are formed in the presence of ligand excess, whereas the complete conversion of L in binuclear complexes can be achieved in the presence of metal excess. The stability data and the electronic spectra suggest a similar coordination environment of the metal centres in all the complexes, each Ni^{II} being coordinated to three of the amine groups in the ligand. At pH close to 7, complex formation occurs in a single kinetic step both for the mono- and the bi-nuclear species, which indicates that coordination of both metal ions to the macrocycle occurs with statistically controlled kinetics. The resolved rate constants for reaction of Ni^{II} with the protonated forms of the ligand are close to those found for related open-chain polyamines of similar steric requirements thus showing that the macrocycle is flexible enough to allow a rapid structural reorganization during the complex formation processes.

Introduction

Polyaza macrocycles and cryptands containing two polyamine sub-units linked by adequate spacers favour the formation of binuclear metal complexes in which both metal centres are placed close to each other. The structure, stability and ability of the resulting complexes for the selective recognition of anions have been the subject of comprehensive work.[1–3] In the past few years, we have been interested in the kinetic effects associated with the proximity of the metal centres in this kind of complex and studied some reactions involving the Cu^{II} complexes of the ligand 3,6,9,17,20,23-hexaazatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11(30),12,14,25(26),27-hexaene (L) and related macrocycles and cryptands.[4–9] It was found that dissociation of the metal ions from the binuclear complexes is statistically controlled, *i.e.* the rate of dissociation of the first ion is double the rate corresponding to the second one.[5–7] There is, however, an important effect of small ancillary ligands as OH^-, NCS^- or N_3^- on the lability of the Cu^{II}–N bonds that may lead to a change in the rate law.[9] In strongly basic solutions, the kinetics of complex formation are also statistically controlled, which confirms that these ligands are flexible enough to reorganize rapidly during the processes of complex formation and dissociation.[6] However, a previous study in slightly acidic media (acetate buffer) revealed that the formation of Cu^{II}-hydroxo and Cu^{II}-acetate complexes led to a complex mixture of species in solution that complicates the analysis of the kinetic data.[4] In order to simplify the analysis of kinetic data for complex formation under moderately acidic conditions, we decided to study the formation of Ni^{II} complexes in aqueous solution at pH close to 7 using MES [2-(4-morpholino)ethanesulfonic acid] and MOPS [3-(4-morpholino)propanesulfonic acid] buffers. Under these conditions, the metal ion exists exclusively as $Ni(H_2O)_6^{2+}$ and the kinetics of reaction with some of the protonated forms of the ligand can be studied.

Table 1 Logarithms of equilibrium constants for the system Ni^{II}–L in aqueous solution (25.0 °C, 0.10 mol dm^{-3} $KClO_4$). The numbers in parentheses represent the standard deviation in the last significant digit

K	Equilibrium quotient	log K
K_{HL}	[HL]/[L][H]	9.49(3)
K_{H_2L}	[H_2L]/[HL][H]	8.65(1)
K_{H_3L}	[H_3L]/[H_2L][H]	7.88(3)
K_{H_4L}	[H_4L]/[H_3L][H]	7.03(2)
K_{H_5L}	[H_5L]/[H_4L][H]	3.54(8)
K_{H_6L}	[H_6L]/[H_5L][H]	3.4(1)
K_{NiL}	[NiL]/[Ni][L]	11.2(1)
K_{HNiL}	[HNiL]/[NiL][H]	7.67(4)
K_{H_2NiL}	[H_2NiL]/[HNiL][H]	6.21(7)
K_{Ni_2L}	[Ni_2L]/[NiL][Ni]	4.0(2)
K_{Ni_2LOH}	[Ni_2LOH][H]/[Ni_2L]	−6.49(8)

Results and discussion

The stability of Ni^{II}–L complexes

The equilibrium constants derived from potentiometric data for protonation of L and complexation of Ni^{II} in aqueous solution are included in Table 1. The log K values for ligand protonation agree well with previous reports,[4,5,10–13] and the stability constants of the Ni^{II} complexes are reasonable when compared to the results obtained for the Cu^{II}–L complexes[4,5,10,12–14] and the Ni^{II} complexes of related ligands.[15] However, the log K value of 11.2 for NiL^{2+} is smaller than the value reported (13.65) for the Ni^{II} complex of the related macrocycle O-bisdien,[16] for which it has been proposed that both dien sub-units in the macrocycle participate in coordination to the metal ion. In contrast, the NiL^{2+} value is closer to that found[15] for $Ni(dien)^{2+}$ (10.5), which strongly suggests that the metal ion is coordinated only to one of the dien sub-units of L, a conclusion similar to that previously achieved for the Cu^{II}–L complexes.[4,5,10,12–14] The different behaviour of L and O-bisdien is probably caused by the higher flexibility of the latter macrocycle.[16]

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† Electronic supplementary information (ESI) available: species distribution curves, calculated spectra, primary kinetic data and deduction of eqn. (5). See http://www.rsc.org/suppdata/dt/b2/b205839c/

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The species distribution curves for solutions containing Ni^{II} and L in 1:1 and 2:1 molar ratios are shown in Figs. 1S and 2S (ESI†). For a 1:1 ratio, the major species in basic solutions is NiL^{2+} and there is no complex formation at pH values lower than 4.5. At intermediate pH values the composition of the solution is more complicated, with mixtures of species that include different amounts of H_2NiL^{4+}, $HNiL^{3+}$ and NiL^{2+}. The data in Table 1 also indicate the formation of stable binuclear Ni_2L^{4+} and $Ni_2L(OH)^{3+}$ species, the hydroxo complex being the major species at pH > 7 in solutions with a 2:1 molar ratio. Although these binuclear Ni^{II} species were not detected for O-bisdien,[16] similar species have been found in the analysis of potentiometric data corresponding to related macrocycles and cryptands.[17–20]

The electronic spectra calculated for the different species formed in aqueous solution are very similar, with a band close to 370 nm (Table 1S, ESI†) and a weaker broad band centred at *ca.* 700 nm. There is also another band whose maximum falls outside the measuring range of the spectrophotometer used (λ_{max} > 800 nm). These spectra are typical of an octahedral (or distorted octahedral) coordination environment about the Ni^{2+} ions.[21] The shift of the band from its position in $Ni(H_2O)_6^{2+}$ (395 nm) is a consequence of macrocycle coordination and, as its position is similar for all the Ni^{II}–L species, the same coordination mode of L can be assumed for all the complexes. As previously commented, the equilibrium data suggest a tridentate coordination of L and, actually, a band at *ca.* 360 nm is observed for other $Ni(amine)_3(H_2O)_3^{2+}$ complexes, although a band of similar characteristics is also observed for some $Ni(amine)_4(H_2O)_2^{2+}$ complexes.[22] An important observation is that the maximum of the band for the binuclear Ni_2L^{4+} and $Ni_2L(OH)^{3+}$ species does not change significantly with respect to the mononuclear complexes, although the molar absorptivities are doubled, which provides strong evidence that the binuclear complexes contain two equivalent NiN_3O_3 chromophores.

The kinetics of formation of Ni^{II}–L complexes

The species distribution curves indicate that formation of the Ni^{II}–L complexes occurs at pH higher than *ca.* 5, although the complete complexation of the ligand is only achieved at pH higher than 6. As a consequence, the pH range available for kinetic studies on complex formation is limited to 6–8; at lower pH values complex formation is incomplete and occurs under reversible conditions, whereas at a higher pH there is precipitation of nickel hydroxide. Species distribution curves at different Ni:L ratios showed that only mononuclear species are formed in the presence of ligand excess, whereas the reaction products in the presence of an excess of Ni^{II} are the binuclear complexes. For this reason, two series of kinetic experiments were carried out using an excess of each reagent. Independently of the nature of the reaction product (mono- or bi-nuclear complexes), the kinetic traces at different wavelengths could always be well fitted by a single exponential and the values derived for the pseudo-first order rate constant (k_{obs}) are included in Table 2S (ESI†). As the complexation process always occurs with a single kinetic step, the values of k_{obs} measure the rate of formation of the final reaction product, *i.e.* the mononuclear complex in the presence of ligand excess and the binuclear complex in the presence of Ni^{II} excess.

The values of k_{obs} change linearly with the total concentration of the reagent in excess (Fig. 1) and the rate law for complex formation is given by eqn. (1). As shown in Fig. 1, the

$$\text{rate} = k[\text{Ni}]_0[\text{L}]_0 \qquad (1)$$

second order rate constants (Table 2) increase with pH and the dependence is illustrated in Fig. 2, which shows the typical shape of reactions involving acid–base pre-equilibria for one of the reagents.

Table 2 Second order rate constants for the formation of Ni^{II}–L complexes (aqueous solution, 25.0 °C, 0.10 mol dm^{-3} $KClO_4$)[a]

Ni^{II} excess		L excess	
pH	k/mol^{-1} dm^3 s^{-1}	pH	k/mol^{-1} dm^3 s^{-1}
6.12	3.2(1)		
6.34	3.4(1)		
6.52	4.1(1)		
6.88	6.9(1)		
7.09	9.1(2)	6.87	11.5(3)
7.29	15.6(2)	7.08	15.1(3)
7.42	18.6(4)	7.25	20.2(4)
7.63	21.1(3)	7.60	33.1(9)

[a] The numbers in parentheses represent the standard deviation in the last significant digit.

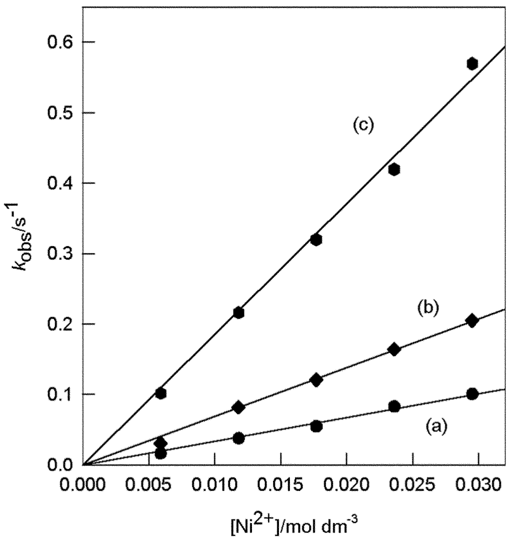

Fig. 1 Plots of kinetic data for the reaction of Ni^{II} with L in aqueous solution under pseudo-first order conditions of metal excess (25.0 °C, 0.10 mol dm^{-3} $KClO_4$, MES or MOPS buffer). The pH values for the different plots are 6.34 (a), 6.88 (b) and 7.42 (c).

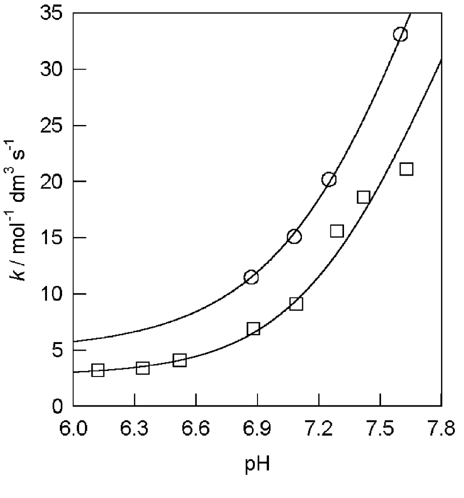

Fig. 2 pH dependence of the second order rate constant for the formation of Ni^{II}–L complexes in aqueous solution. The circles correspond to the formation of mononuclear complexes and the squares to the binuclear complexes. The solid lines have been drawn using the parameters derived from the fit of experimental data to eqn. (5) in the text (see also Fig. 3).

The values of k in the presence of ligand excess directly measure the rate of formation of the mononuclear complexes but the reaction products in the presence of Ni^{II} excess are the binuclear complexes, whose formation requires the successive coordination of two metal ions. As the rate constants for coordination of the first metal ion must be similar to those observed in the experiments with ligand excess, and as formation of the binuclear complexes occurs in a single kinetic step with rate constants smaller than the corresponding k values for the mononuclear complexes (Fig. 2), the most plausible interpretation is to consider that the formation of the binuclear complexes is statistically controlled.[6] In that case, only the rate constants for coordination of the second ion are determined from the experimental curves[23] and the values corresponding to the first one are obtained by doubling the value found for the second ion. A comparison of the kinetic data in Fig. 2 shows that doubling the k values in the presence of a Ni^{2+} excess leads to values close to those found in the presence of ligand excess. The observation of statistical kinetics also requires that the molar absorptivity of the mononuclear intermediate formed during the conversion of L in the binuclear complex be the mean value of those corresponding to the starting reagent and the final product. The ε values in the calculated spectra show that this condition is fulfilled both at the d–d absorption band of the complexes and at the measuring wavelength (290 nm).

Under the conditions of the kinetic experiments, the only nickel species at relevant concentrations is Ni^{2+} but the ligand exists as a mixture of H_4L^{4+}, H_3L^{3+} and H_2L^{2+}. Complex formation may occur through the three pathways indicated in eqns. (2)–(4) and the relative contribution of each pathway to

$$Ni^{2+} + H_4L^{4+} \longrightarrow NiL^{2+} + 4H^+; \quad k_{H_4L} \tag{2}$$

$$Ni^{2+} + H_3L^{3+} \longrightarrow NiL^{2+} + 3H^+; \quad k_{H_3L} \tag{3}$$

$$Ni^{2+} + H_2L^{2+} \longrightarrow NiL^{2+} + 2H^+; \quad k_{H_2L} \tag{4}$$

the net rate of reaction changes with pH. Although the reaction product is a mixture of mono- and bi-nuclear species whose composition depends on the reaction conditions (pH, Ni or L excess), only the mononuclear NiL^{2+} species is included in eqns. (2)–(4) for simplicity.

The values of k_{H_4L}, k_{H_3L} and k_{H_2L} can be estimated from the pH dependence of k using eqn. (5) (Appendix 1, ESI†) and

$$k(1 + K_{H_3L}[H^+] + K_{H_3L}K_{H_4L}[H^+]^2) = k_{H_2L} + k_{H_3L}K_{H_3L}[H^+] + k_{H_4L}K_{H_3L}K_{H_4L}[H^+]^2 \tag{5}$$

the previously determined equilibrium constants for ligand protonation.

The plot according to eqn. (5) of the data for experiments in the presence of Ni^{II} excess is included in Fig. 3 and the analysis of the data leads to $k_{H_2L} = 65 \pm 11$, $k_{H_3L} = 5.7 \pm 1.3$ and $k_{H_4L} = 2.7 \pm 0.2$ (all in units of $mol^{-1}\ dm^3\ s^{-1}$). A similar treatment of the data in the presence of ligand excess leads to values of $k_{H_2L} = 81 \pm 6$, $k_{H_3L} = 13.7 \pm 2.2$ and $k_{H_4L} = 4.9 \pm 1.3$ (also in units of $mol^{-1}\ dm^3\ s^{-1}$), although in this case the set of experimental data are clearly incomplete and the values must be considered only as being approximate. As expected for statistical kinetics, the values of the resolved rate constants in the presence of ligand excess, especially k_{H_3L} and k_{H_4L}, are double the values derived from experiments with metal excess, the differences being easily understood in terms of experimental and calculation errors. The larger difference observed for k_{H_2L} is surely caused because H_2L^{2+} is a minor species at the pH range of the kinetic experiments and so its contribution to the net rate of reaction is the worst defined. It is also important to note that the resolved rate constants derived for the Ni^{II}–L complexes are close in all cases to those found for reaction of Ni^{2+} with the partially protonated forms of open-chain polyamines with similar steric requirements.[24–27]

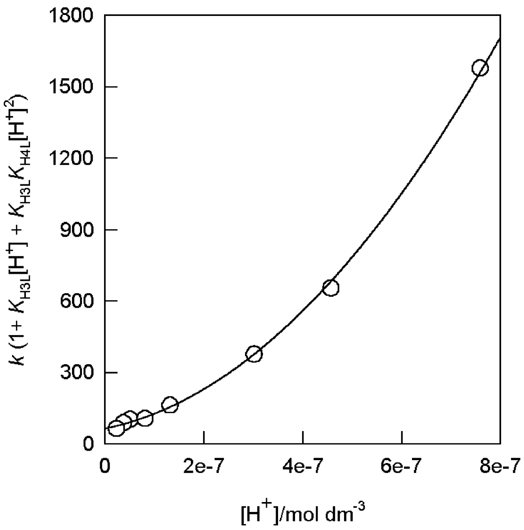

Fig. 3 Plot of kinetic data for the formation of Ni^{II}–L complexes according to eqn. (5) in the text. The plot corresponds to data under pseudo-first order conditions of metal excess.

The mechanism of formation of the Ni^{II}–L complexes

The formation of metal complexes from solvated Ni^{2+} ions is accepted to occur through the Eigen–Wilkins mechanism, the values of the second order rate constant being usually in good agreement with theoretical values calculated from the product $K_{os}k_{ex}$, where K_{os} is obtained from the Fuoss equation and k_{ex} represents the rate constant for solvent exchange. In some cases, an apparent steric factor (ρ) must be included to account for the fact that not all the ligand configurations in the outer-sphere complex have the donor atom with the orientation required for coordination.[28] The values of ρ for amines of different steric requirements have been previously reported.[29]

For the case of polydentate ligands, the mechanism can be more complicated because complex formation involves several consecutive substitutions and the rate-determining step can be the formation of the first metal–ligand bond or can be displaced to the formation of one of the subsequent bonds. Rorabacher and co-workers[29] have proposed the use of the ρ values as a criterion to determine the rate-determining step in these reactions of polydentate ligands. Theoretical values of ρ are calculated by adding the contributions estimated for each donor atom in the ligand and the values are then compared with those calculated using eqn. (6) and the experimental value

$$\rho_{exp} = \frac{4k}{3K_{os}k_{ex}} \tag{6}$$

of k. The values of ρ_{theor} and ρ_{exp} are close to each other when the rate-determining step corresponds to first bond formation, whereas values of ρ_{exp} which are significantly smaller than ρ_{theor} indicate a shift in the rate-determining step to a later point along the reaction coordinate. In some cases, the ρ_{exp} values are larger than those of ρ_{theor}, which has been interpreted in terms of an internal conjugate base (ICB) effect.[30]

In order to obtain ρ_{exp} values for the protonated forms of macrocycle L, the values of K_{os} must be estimated with the Fuoss equation, but the estimations depend on the charge of the species and reasonable doubt on the actual charge exists in cases as H_2L^{2+}, H_3L^{3+} and H_4L^{4+}, where the positive charges are located on several donor atoms distributed over a large macrocycle. As formation of the Ni^{II}–L complexes occurs with statistically controlled kinetics, the dien sub-units behave independently and we consider it more reasonable to use a +1 or +2 charge for the $Hdien^+$ and H_2dien^{2+} sub-units in H_2L^{2+}, H_3L^{3+} and H_4L^{4+} instead of the total charges of the ions. With these values for the charge and a separation between the reagents in the outer-sphere complex similar to that proposed for related ligands,[24] the estimated value of K_{os} is 0.062 for the $Hdien^+$ sub-units and 0.032 for the H_2dien^{2+} sub-units. Using these K_{os} values and $k_{ex} = 3.15 \times 10^4\ s^{-1}$ for water exchange,[31] the ρ_{exp} values derived from the data in the presence of Ni^{2+} and L excess for H_4L^{4+} (two H_2dien^{2+} sub-units) are 0.007 and 0.006, respectively. The reaction of H_3L^{3+} with the first Ni^{2+} must occur preferably through the $Hdien^+$ sub-unit and the resulting values of ρ_{exp} are 0.008 (Ni^{2+} excess) and 0.009 (L excess). For the case of H_2L^{2+} (two $Hdien^+$ sub-units), the values of ρ_{exp} for coordination of the first metal ion are 0.089 (Ni^{2+} excess) and 0.055 (L excess).

The values of ρ_{theor} can be obtained assuming a contribution of 0.006 for each nitrogen donor,[29] which leads to 0.012, 0.018 and 0.024 for coordination of the first Ni^{2+} to H_4L^{4+}, H_3L^{3+} and H_2L^{2+}, respectively. In all cases, the experimental and theoretical values of ρ only differ by a factor of 2–4, which indicates that the protonated forms of L react with Ni^{2+} at rates close to the values estimated from the product $K_{os}k_{ex}\rho$ using previously reported k_{ex} and K_{os} values and the estimation of the steric effects proposed by Rorabacher and co-workers.[29]

As a summary, the kinetic results for reaction of Ni^{2+} with the protonated H_4L^{4+}, H_3L^{3+} and H_2L^{2+} species are consistent with rate-determining formation of the first metal–ligand bond and there is no evidence of ICB acceleration or any kinetic effect associated with the macrocyclic structure of the ligand. Despite the proximity of the metal ions and the positive charges on the ligand, the rate of coordination of both metal centres is also statistically controlled at neutral pH, which confirms our previous observations[5–8] in the sense that both dien subunits behave independently and that this kind of ligand is flexible enough to reorganize rapidly during the processes of complex formation and decomposition.

Experimental

The ligand 3,6,9,17,20,23-hexaazatricyclo[23.3.1.1^{11,15}]triaconta-1(29),11(30),12,14,25(26),27-hexaene (L) was synthesized as L·6HBr following the literature procedure.[10] The $Ni(ClO_4)_2$ salt was prepared from nickel carbonate hydroxide tetrahydrate and $HClO_4$. All other reagents were obtained from Aldrich and used without further purification.

Equilibrium experiments

The KOH solutions used for the potentiometric titrations were obtained from Aldrich and titrated with potassium hydrogenphthalate. The pH readings were obtained with a Crison 2002 instrument provided with an Ingold combined electrode and calibrated to read pH as $-\log [H_3O^+]$ according to the procedure recommended by Martell and Motekaitis.[32] Solutions of Ni^{II} were prepared from $Ni(ClO_4)_2$ and titrated with EDTA using murexide as indicator.

The protonation constants of the ligand and the formation constants of the Ni^{II}–L complexes were determined from potentiometric titrations carried out at 25.0 °C under N_2 with solutions containing L and Ni^{II} at different molar ratios: 1:0, 1:1 and 1:2 (L:Ni). Two sets of titrations were carried out to check the reproducibility of the results and to obtain an estimate of the errors in the reported values of the stability constants. The ligand concentration was always in the range $(1–2) \times 10^{-3}$ mol dm^{-3}, and the concentration of Ni^{II} was then adjusted to the desired molar ratio. The initial volume was always close to 50.0 cm^3, and the ionic strength was adjusted to 0.10 mol dm^{-3} with $KClO_4$. The number of points measured was different for every titration, although there were at least 10 points for each neutralization of a proton or hydrolytic reaction. The range of pH expands from *ca.* 3 to 11, except for the titration with a 2:1 molar ratio in which precipitation occurs at pH close to 8. The data were analysed with the program BEST[32] assuming a pK_w value of 13.78 and the species distribution curves were obtained with programs SPE and SPEPLOT.[32]

In order to obtain information about the spectra of the complexes in aqueous solution, several spectra were recorded at different pH values for solutions containing Ni^{II} and L in 1:1 and 2:1 molar ratios. From those spectra and the stability constants previously derived from the potentiometric titrations, the spectra of the mono- and bi-nuclear Ni^{II}–L complexes formed in aqueous solution were calculated.

Kinetic experiments

The experiments were carried out at 25.0 °C with an Applied Photophysics stopped-flow instrument. The ionic strength of the solutions was adjusted to 0.10 mol dm^{-3} by adding the required amount of $KClO_4$. All experiments were carried out under pseudo-first order conditions of ligand or metal excess, and kinetic traces were fitted by a single exponential using the standard software of the stopped-flow instrument. The wavelength was selected at 290 nm in preliminary spectral scanning experiments that were also used to check the independence of the observed rate constants with the changes in the concentration of the limiting reagent. The actual concentration of each reagent and the buffer used are indicated in Table 2S. The reported values of the rate constants correspond to the mean value for at least five determinations.

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