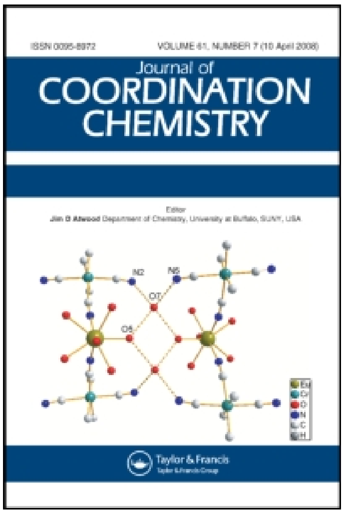

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KINETICS AND MECHANISM OF DISSOCIATION OF SOME BIS-(N^1-SUBSTITUTED BIGUANIDE) COMPLEXES OF NICKEL(II) IN AQUEOUS ACID

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The rates of dissociation of bis-(N^1-methylbiguanide)nickel(II) and bis-(N^1-phenylbiguanide)nickel(II) in aqueous acid have been studies by the stopped-flow spectrophotometric technique. The reactions occur in two consecutive steps, the first being faster than the second, ultimately forming the aquometal ion and the protonated ligand. For each step the rate is acid dependent as expressed by $k_x = k'_x[H^+]$, where k_x is the observed rate constant. The results are consistent with a mechanism involving an assisted dissociative process involving the protonated complexes with considerable solvent participation in the transition state. The observed lability order is $Ni(PhbigH)_2^{2+} > Ni(MebigH)_2^{2+} > Ni(BigH)_2^{2+}$.

INTRODUCTION

Biguanide complexes of bi- and trivalent metal ions, while having exceptional thermodynamic stability,[1] dissociate fairly easily in acid media due to the availability of a favourable reaction path involving protonation of the ligand.[2-6] Comparative studies have been made on the dissociation of a series of biguanide and N^1-substituted biguanide complexes of trivalent metal ions in aqueous acid solution.[2-4] Studies have also been extended to complexes of bivalent metal ions, *viz.*, the bis(biguanide)palladium(II)[5] and bis(biguanide)nickel(II) complexes,[6] and ethylenebisbiguanide complexes of nikel(II) and copper(II).[6] Such studies on substituted biguanide complexes of bivalent metal ions appeared worthy of investigation in order to investigate the effect of substituents on theligands towards the labilities of the corresponding complexes. Results of such studies on the N^1-methyl- and N^1-phenylbiguanide complexes of nickel(II) are presented in this communication and compared with those of the biguanide complex reported earlier.[6]

EXPERIMENTAL

Materials and reagents

The complexes, $Ni(CH_3C_2N_5H_6)_2Cl_2.4.5H_2O$[7] and $Ni(C_6H_5C_2N_5H_6)_2Cl_2.2.5H_2O$[8] (where $CH_3C_2N_5H_6$ = N^1-methylbiguanide and $C_6H_5C_2N_5H_6$ = N^1-phenylbiguanide) were prepared by known methods and their purity was checked by elemental analysis. All other chemicals used were either of reagent grade or else purified by known methods. Solutions were prepared using doubly distilled water and stored in resistant glass vessels.

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Apparatus and Procedure

The spectra of freshly prepared aqueous solutions of these complexes were recorded using a VSU-2P (Carl-Zeiss) spectrophotometer. Both complexes have fairly broad absorption bands with the following characteristics which agreed reasonably with the values reported in literature.[1] $Ni(CH_3C_2N_5H_6)_2^{2+}$: λ_{max} = 465 nm, ϵ_{max} = 55 M^{-1} cm^{-1}; $Ni(C_6H_5C_2N_5H_6)_2^{2+}$: λ_{max} = 460 nm, ϵ_{max} = 65 M^{-1} cm^{-1}.

The rates of dissociation of the complexes (0.002M) in aqueous solution containing varying amounts of acid, HCl (0.02M to 0.04M) and KCl (to adjust the ionic strength to 0.1M) were studied spectrophotometrically using absorbance measurements at the λ_{max} of the complex (where the reaction products are virtually non-absorbing at the concentrations used) using a Canterbury SF-3A stopped-flow spectrophotometer, provided with an oscilloscope (OS 1000A) and a transient recorder (Datalab DL 901) system. The cell was thermostated in order to maintain the desired temperature (± 0.05°). From the observed changes in absorbance with time, the rate constants k_f and k_s were evaluated using known procedures for a two-step process.[9] For all the experiments the most reproducible curves were analysed and the constants k_f and k_s were evaluated by the method of least-squares.

RESULTS AND DISCUSSION

Detailed analysis by a known procedure[9] of the absorbance-time changes for the reactions revealed that these complexes undergo dissociation in two consecutive steps; an initial faster reaction (k_f) is followed by a relatively slower one (k_s). Both show first-order dependence on acid concentration. This can be interpreted by a mechanism proposed earlier[6] in which the initial (faster) step involves protonation of the metal bound ligand[3] in a fast equilibrium followed by bond rupture in the rate determining step leading to the formation of the monobiguanide complex and releasing one biguanidium ion. The second (slower) step is a repetition of the process in the first step, involving loss of the remaining ligand, and forming the aquometal ion as the final product. Indeed, the existence of such monbiguanide complexes, believed to be formed in the first step, have been established earlier in a few cases,[10] and this lends support to the proposed mechanism. Protonation of the bound biguanide ligand can be explained on the basis of the known structure[11,12] of biguanide complexes and this process would facilitate the dissociation of the metal-ligand bond as discussed earlier.[2-4,6]

Based on the mechanism proposed above, the observed pseudo-first-order rate constants for each step *i.e.*, k_f and k_s, will show acid dependence as shown in equation (1),

$$k_x = k'_x[H^+] \qquad (1)$$

where x refers to "f" or "s", as the case may be.

From the specific rate constant values obtained at three different temperatures (20, 25 and 30°) for each step, the corresponding activation parameters have been evaluated by making use of the Eyring equation[13] (see Table 1).

For the three biguanide complexes, the relative rates of dissociation for either path, corresponding to k_f and k_s, are given in Table II (data at 25°). The results show that at any particular temperature the rates of dissociation of the different complexes for each of the steps decrease in the sequence $Ni(PhbigH)_2^{2+} > Ni(MebigH)_2^{2+} > Ni(BigH)_2^{2+}$.

This may be explained on the basis of steric effects of the substituent in the biguanide. The increased strain due to a bulkier substituent causes a destabilisation of the chelate ring and consequently a higher rate of dissociation. This is in contrast to what has been observed[2] in the case of the biguanide complexes of trivalent metal ions such as Co(III)

TABLE I
Kinetic parameters for the acid catalysed dissociation of the complexes.

	Temp. (°)	Ionic strength[a]	$10^{-3}k'_x/M^{-1}s^{-1}$	
			k_s	k_f
$Ni(MebigH)_2^{2+}$	20	0.1	3.12 ± 0.09	4.44 ± 0.32
	25	0.1	3.84 ± 0.11	5.82 ± 0.15
	25	0.05	3.10 ± 0.20	4.00 ± 0.30
	30	0.1	4.98 ± 0.16	7.54 ± 0.21
	$\Delta H^{\neq}/kJ\ mol^{-1}$		32.3 ± 1.7	37.0 ± 0.4
	$\Delta S^{\neq}/J\ K^{-1}\ mol^{-1}$		−68.9 ± 5.5	−50.4 ± 0.8
$Ni(PhbigH)_2^{2+}$	20	0.1	7.14 ± 0.07	9.46 ± 0.30
	25	0.1	7.91 ± 0.16	10.80 ± 0.64
	25	0.05	6.23 ± 0.30	9.00 ± 0.20
	30	0.1	8.88 ± 0.32	11.98 ± 0.52
	$\Delta H^{\neq}/kJ\ mol^{-1}$		13.9 ± 0.4	15.1 ± 0.8
	$\Delta S^{\neq}/J\ K^{-1}\ mol^{-1}$		−125.6 ± 1.7	−119.7 ± 2.5

[a] HCl + KCl, in mol dm^{-3}.

TABLE II
Relative rates of dissociation at 25° of biguanide[6] and N^1-substituted biguanide[14] complexes of nickel(II).

	$[Ni(PhbigH)_2]^{2+}$	$[Ni(MebigH)_2]^{2+}$	$[Ni(BigH)_2]^{2+}$
k_f path	1	0.49	0.29
k_s path	1	0.54	0.34

and Cr(III) where the rate of dissociation increases with an increase in basicity of the ligand according to the sequence biguanide > methylbiguanide > phenylbiguanide. This apparent paradox is possibly due to the fact that k'_x is a product of an equilibrium constant (K) for protonation of the complex and a rate constant (k) for the transformation of the protonated complex. For inert metal ions like Co(III) and Cr(III), K may reasonably by expected to be appreciably larger than k so that the former is in control of the overall rate constant (kK) and hence the rate will follow the sequence of increasing basicity of the ligand. However for a labile metal ion such as Ni(II) the reverse is obviously true; here k is likely to be appreciably larger than K and hence controls the overall rate.

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