

# Kinetics of ternary complex formation with the (nitrilotriacetato)zinc(II) complex: the effect of buffers and pH

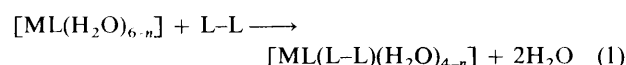
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The temperature-jump relaxation method has been used to measure rate constants for the formation ( $k_f$ ) and dissociation of ternary complexes between 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine and 5-nitrosalicylate (2-) ( $\text{nsa}^{2-}$ ), respectively, and  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})]^-$  [ $\text{nta}$  = nitrilotriacetate(3-)]; also for proton transfer between  $\text{Hnsa}^-/\text{nsa}^{2-}$  and various buffers. The effects of pH and buffer on the ternary complexation kinetics have been investigated, and independent equilibrium constants are reported for the formation of several  $[\text{Zn}(\text{nta})\text{B}]$  (B = buffer) complexes. Values of  $k_f$  for bipy and  $\text{nsa}^{2-}$  are similar to those for the corresponding reactions of cobalt(II).

The rate constants for the formation and dissociation of most substitution-labile 1:1 metal complexes in aqueous solution ( $k_f$  and  $k_d$ , respectively) can be predicted quite reliably if the effective stability constant  $K^c$  ( $= k_f/k_d$ ) is known.<sup>1,2</sup> Much less is known about analogous reactions involving metal ions in which some of the water molecules of the inner hydration sphere have already been replaced by other co-ordinating groups. It is important to gain an understanding of the factors controlling the kinetics of such ternary complex formation since many catalytic reactions are of this type, including many involving zinc metalloenzymes.<sup>3</sup>

The metal cation  $\text{M}^{2+}(\text{aq})$  whose ternary complexes have been most widely studied kinetically is nickel(II), and we have recently found<sup>4</sup> that the effect of a particular bound  $n$ -dentate ligand L on its reactivity towards a second ligand L-L [as in reaction (1), from which charges have been omitted, with M =



Ni] can be described by a simple parametrization scheme. Using the same sets of charged and neutral ligands L and L-L, we have also observed<sup>5</sup> a similar pattern for the corresponding reactions of cobalt(II). The present paper is the first step in the extension of this comparative approach to the reactions of zinc.

Early results indicated that the kinetics of zinc ternary complex formation can be influenced greatly by pH and by the nature and concentration of the buffer used. We argued that such pH and buffer effects would be easiest to analyse in a relatively well characterized system where the metal ion did not change its co-ordination number during the reaction as, for example, with reaction (1) (M = Zn,  $n = 4$ ) where L is a quadridentate ligand. There is literature evidence<sup>6</sup> that the 1:1 complex between  $\text{Zn}^{2+}(\text{aq})$  and nitrilotriacetate (3-) ( $\text{nta}^{3-}$ ) is octahedral and we therefore chose to investigate the reactivity of this complex first.†

## Experimental

The zinc solutions were prepared either from A. R. zinc oxide (Fisons) with the stoichiometric amount of HCl (Koch-Light,

A. R. 35%) or from  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Fisons, A. R.); they were standardized against the disodium salt of ethylenediamine- $N,N,N',N'$ -tetraacetic acid ( $\text{H}_4\text{edta}$ ) using xylenol orange as indicator.<sup>7</sup> 2,4,6-Trimethylpyridine (tmpy) (Fisons) was purified by fractional distillation, 5-nitrosalicylic acid ( $\text{H}_2\text{nsa}$ ) (Fluka) by double recrystallization from water, and imidazole (Fisons) by recrystallization from benzene and then water. Nitrilotriacetic acid (Fluka), 2,2'-bipyridine (bipy) (BDH), 4,4'-dimethyl-2,2'-bipyridine (dmbipy) (Koch-Light), and triethylamine and tris(hydroxymethyl)methylamine (Tris) (Fisons) were all used without further purification.

The solutions for kinetic and equilibrium measurements were made up with triply distilled water, the middle distillation being from alkaline potassium permanganate. The pH was adjusted with concentrated NaOH and HCl or  $\text{HNO}_3$ , depending on the source of the zinc (although the results appeared to be independent of the latter). The pH measurements were made on a Radiometer PHM 26c with GK 2321 semimicro dual electrode, and sodium-ion corrections were applied at high pH according to the manufacturer's nomogram. An ionic strength of  $0.30 \text{ mol dm}^{-3}$  was maintained with NaCl or  $\text{NaNO}_3$ , respectively. Solutions of bipy and dmbipy ( $ca. 10^{-3} \text{ mol dm}^{-3}$ ) were freshly made by addition of equimolar acid to the weighed material and with gentle warming. The concentration of the bipy solution was checked spectrophotometrically.<sup>8</sup> Temperatures were accurate to better than  $\pm 0.1^\circ\text{C}$ .

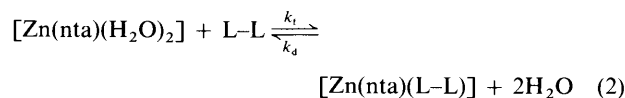
Kinetic (temperature-jump) and equilibrium (UV/VIS spectrophotometric) measurements were undertaken by standard methods,<sup>9,10</sup> except as described below. The data were generally obtained at 380 (nsa) or 308 nm (bipy, dmbipy), although identical results were obtained at several other wavelengths for each system. Each data point is the average of five or six separate determinations with the same solution. Published stability constants and  $\text{p}K_a$  values,<sup>11</sup> together with an interpolated value<sup>12</sup> of 13.90 for  $\text{p}K_w$  ( $20^\circ\text{C}$ ,  $I = 0.30 \text{ mol dm}^{-3}$ ), were used to calculate the concentrations of the various species present at the different total concentrations of Zn and nta and pH values. The ratio of weighed-in concentrations nta:Zn was generally in the range 1.03–1.08:1 and it was always possible to eliminate the relaxation effects associated with free  $\text{Zn}^{2+}$  and  $[\text{Zn}(\text{nta})_2]^{4-}$ . The weighed-in concentrations of bipy, dmbipy and nsa were generally in the range  $5.0 \times 10^{-5}$ – $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ .

## Results

In the temperature-jump relaxation method the position of

† Charges on individual complexes are indicated except where this could lead to ambiguity. Thus, the six-co-ordinate zinc-nta complex is generally represented as  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  but in an equation describing its reaction with the ligand L-L the charge is omitted;  $[\text{Zn}(\text{nta})]$  represents the stoichiometric mixture of  $\text{Zn}^{2+} + \text{nta}^{3-}$  comprising the aqua and hydroxo forms of the zinc-nta complex.

equilibrium is changed by means of a sudden temperature rise. The new equilibrium condition is approached exponentially and the relaxation time  $\tau$  is a function of the rate constants of the reaction(s) involved. For the isolated, single-step reaction (2) involving a bidentate ligand L-L (charges omitted) the



relaxation expression is given by equation (3), where  $c_{\text{ML}}$  and

$$\tau^{-1} = k_r(c_{\text{ML}} + c_{\text{L-L}}) + k_d \quad (3)$$

$c_{\text{L-L}}$  are the (new) equilibrium concentrations of free  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  and free L-L, respectively. Under pseudo-first-order conditions in  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  this reduces to equation (4), and  $k_r$  and  $k_d$  can be evaluated from the slope and

$$\tau^{-1} = k_r c_{\text{ML}} + k_d \quad (4)$$

intercept, respectively, of a straight-line plot of  $\tau^{-1}$  against  $c_{\text{ML}}$ . Where either or both of the reactants in equation (2) is involved in other reactions it may be necessary to modify equations (3) and (4). The new form of the relaxation expression then depends on the nature of the additional step(s) and their relaxation time(s) compared with that of reaction (2). The additional steps which concern us here are (a) the deprotonation of  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$ , (b) the protonation of L-L =  $\text{nsa}^{2-}$  and (c) the formation of competing ternary complexes involving the buffer.

We have arranged the results in four sections: (i) the kinetics of ternary complex formation with bipy and dmbipy {these measurements have also been used to determine the  $\text{p}K_a$  of  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$ }; (ii) the kinetics of ternary complex formation with  $\text{nsa}^{2-}$  (the full analysis of these results requires information from the other three sections); (iii) the kinetics of deprotonation of  $\text{Hnsa}^-$  using various buffers and (iv) the measurement of equilibrium constants for the formation of ternary complexes involving zinc, nta and the buffer {these have been determined spectrophotometrically using  $[\text{Zn}(\text{nta})(\text{nsa})]^{3-}$  as indicator}.

#### (i) Ternary complexes with bipy or dmbipy; $\text{p}K_a$ of $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$

The variation of  $\tau^{-1}$  with concentration and pH is given in Table 1. While the dependence of  $\tau^{-1}$  on  $[\text{Zn}(\text{nta})]$  (the analytical concentration of the 1:1 zinc-nta complex) at constant pH (for bipy) is linear, a plot of  $\tau^{-1}$  vs. pH at constant  $[\text{Zn}(\text{nta})]$  (not shown) has the form of a standard titration curve, the value of  $\tau^{-1}$  tending towards zero at high pH. In view of the reports<sup>13,14</sup> that  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  has a  $\text{p}K_a$  value of about 10.3, the simplest interpretation of this behaviour is to assume that the aqua form can react with bipy or dmbipy to produce the ternary complex but the hydroxo form, presumably  $[\text{Zn}(\text{nta})(\text{OH})(\text{H}_2\text{O})_2]^{2-}$ , cannot.

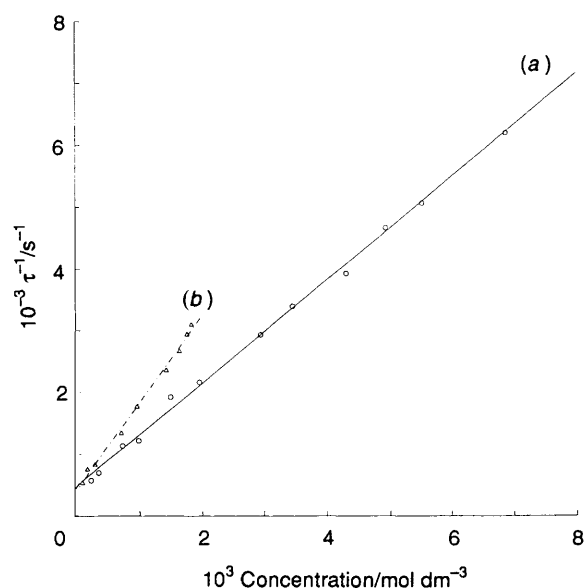
If this is correct, a plot of  $\tau^{-1}$  vs. the concentration of the aqua form under pseudo-first-order conditions should produce a straight line [equation (4)], since the pH was invariably well above the  $\text{p}K_a$  of bipy (4.44<sup>11</sup>) or dmbipy (5.32<sup>11</sup>) and in the well buffered solutions used the deprotonation of  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  is<sup>15</sup> fast compared to the formation of the ternary complex. Fig. 1(a) shows such a plot for the bipy reaction.

For the dmbipy reaction the conditions were not pseudo-first order and it is necessary to use an extended form of the relaxation expression. Although the protonation of dmbipy can be neglected, equation (3) must be modified to take account of the deprotonation of the aqua complex. The appropriate

**Table 1** Variation<sup>a</sup> in  $\tau^{-1}$  with concentration and pH for the reaction of  $[\text{Zn}(\text{nta})]$  with (i) bipy and (ii) dmbipy

(i) Reaction with bipy				(ii) Reaction with dmbipy <sup>b</sup>	
$[\text{Zn}]/10^{-3}$ mol dm <sup>-3</sup>	$[\text{bipy}]/10^{-5}$ mol dm <sup>-3</sup>	pH <sup>c</sup>	$\tau^{-1}/10^3$ s <sup>-1</sup>	pH <sup>d</sup>	$\tau^{-1}/10^3$ s <sup>-1</sup>
0.25	5.0	8.80	0.58	7.39	3.10
0.40	5.0	8.80	0.70	8.43	2.94
0.80	5.0	8.80	1.14	9.15	2.67
1.00	8.0	7.60	1.22	9.59	2.36
1.60	5.0	8.80	1.93	10.17	1.77
2.00	8.0	7.15	2.17	10.43	1.34
2.40	5.0	8.80	2.65	10.99	0.83
3.00	8.0	7.20	2.94	11.23	0.76
3.50	4.0	7.20	3.40	11.58	0.54
4.50	8.0	8.10	3.92		
5.00	5.7	7.21	4.66		
5.60	6.4	7.30	5.06		
7.00	8.0	7.20	6.20		

<sup>a</sup> Data refer to 20 °C and ionic strength 0.3 mol dm<sup>-3</sup> (NaCl);  $[\text{Zn}]$  is the weighed-in concentration of zinc. <sup>b</sup>  $[\text{Zn}] = 2.0 \times 10^{-3}$ ,  $[\text{dmbipy}] = 2.0 \times 10^{-5}$  mol dm<sup>-3</sup>. <sup>c</sup> The pH was maintained by  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> tmpy buffer (pH 8.80) or  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> Tris. <sup>d</sup> The pH was maintained by  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> tmpy buffer.



**Fig. 1** Variation of  $\tau^{-1}$  with concentration (see text) for the reaction of  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  with (a) bipy ( $\circ$  and solid line) and (b) dmbipy ( $\triangle$  and dot-dashed line)

relaxation expression is given in equation (5), where  $K_{\text{ML}}$  is the

$$\tau^{-1} = k_r(c_{\text{ML}} + \{c_{\text{L-L}}/[1 + (K_{\text{ML}}/c_{\text{H}})]\}) + k_d \quad (5)$$

acid-dissociation constant of  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  and  $c_{\text{H}}$  the hydrogen-ion concentration. Fig. 1(b) confirms the predicted linearity between  $\tau^{-1}$  and  $c_{\text{ML}} + \{c_{\text{L-L}}/[1 + (K_{\text{ML}}/c_{\text{H}})]\}$ . The individual abscissa values were obtained by iteration using the ternary stability constant evaluated from the ratio of the slope ( $= k_r$ ) to the intercept ( $= k_d$ ). Since they also depend critically on the value assumed for the  $\text{p}K_a$  of the zinc aqua complex the linearity of the plot can be used as a criterion for the determination of the  $\text{p}K_a$ . The best straight line [Fig. 1(b)] is obtained with a  $\text{p}K_a$  of 10.25. The spectrophotometric determination of the  $\text{p}K_a$  of  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  using bipy gave a best-fit value of 10.13 (0.15). The 'best' rate and equilibrium constants are given in Table 2.

**Table 2** Rate and equilibrium constants\* for ternary complex formation involving [Zn(nta)] (estimated errors in parentheses)

	bipy	dmbipy	nsa <sup>2-</sup>
$k_f/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.83 (0.02) $\times 10^6$	1.42 (0.04) $\times 10^6$	7.9 (0.3) $\times 10^6$
$k_d/\text{s}^{-1}$	4.8 (0.5) $\times 10^2$	4.1 (0.5) $\times 10^2$	1.2 (0.1) $\times 10^4$
$\log K_{\text{kin}}$	3.24	3.54	2.82
$\log K_{\text{spec}}$	—	—	3.00

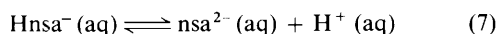
\* Data refer to 20 °C and  $I = 0.3 \text{ mol dm}^{-3}$  (NaCl);  $K_{\text{kin}}$ ,  $K_{\text{spec}}$  are equilibrium constants which have been obtained kinetically and spectrophotometrically, respectively.

### (ii) Ternary complexes with nsa<sup>2-</sup>

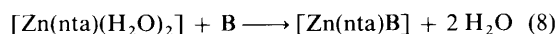
In our studies on complex formation between 5-nitrosalicylic acid and magnesium(II),<sup>16</sup> nickel(II)<sup>17</sup> or cobalt(II)<sup>18</sup> species we sometimes observed a U-shaped pH profile for  $\tau^{-1}$  at constant metal concentration. Similar profiles have been found<sup>19</sup> with other protonated ligands and they can be understood in terms of a two-pathway scheme involving the reaction of the metal species with, respectively, the protonated and deprotonated forms of the ligand. Preliminary work with the present system revealed the absence of a lower arm to the pH profile in well buffered solutions, the value of  $\tau^{-1}$  remaining constant at pH below about 8.2 but increasing at higher pH. From this we conclude that the dianion nsa<sup>2-</sup> is kinetically active but the monoanion Hnsa<sup>-</sup> is not. If we also assume that, as in the reactions with bipy and dmbipy, only the aqua form of the binary complex is active, the appropriate relaxation expression under pseudo-first-order conditions is as given in equation (6), where  $K_{\text{Hnsa}}$  is the acid-dissociation constant of Hnsa<sup>-</sup>.

$$\tau^{-1} = \{k_f c_{\text{ML}}/[1 + (c_{\text{H}}/K_{\text{Hnsa}})]\} + k_d \quad (6)$$

In deriving equation (6) it was assumed that  $c_{\text{H}}$  is kinetically buffered, *i.e.* that the proton-transfer reaction (7) is in



equilibrium throughout the complexation step. If this condition is not fulfilled there will be coupling between reactions (2) ( $\text{L-L} = \text{nsa}^{2-}$ ) and (7) and the data must be analysed in terms of normal modes,<sup>15</sup> which is much more difficult. In the limit, reaction (7) becomes the limiting step in the relaxation process and no kinetic information is available about the complexation step. It is therefore important to try to maintain kinetic buffering of reaction (7) during the relaxation of reaction (2) ( $\text{L-L} = \text{nsa}^{2-}$ ). On the other hand, at the relatively high buffer concentrations needed to ensure this, there could be formation of competing ternary complexes with the high-pH form B of the buffer, as in equation (8) (charges omitted). Of the buffers used,



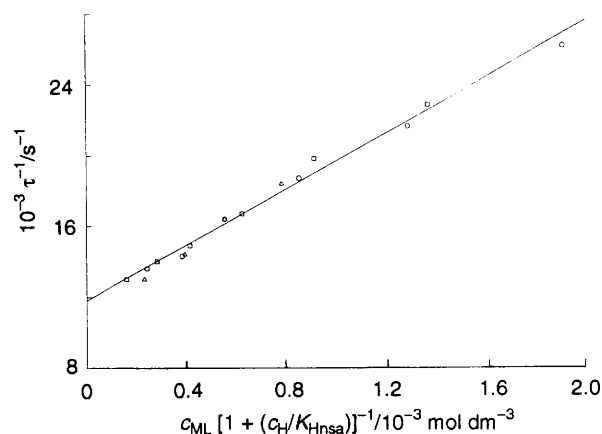
at least Tris and imidazole are known<sup>20</sup> to form 1 : 1 complexes with several transition metals, including zinc.

Preliminary experiments confirmed the need to take both these complications into account. For example, plots of  $\tau^{-1}$  against total buffer concentration at constant [Zn(nta)] and pH (not shown) showed a rapid increase to approximately the same maximum value followed by a more gradual decrease for Tris and tmpy, but a gentle rise towards a much lower maximum for triethylamine. A simple interpretation of these observations is the following. At low buffer concentration reaction (7) is rate-limiting. As the buffer concentration is increased reaction (7) is speeded up (through the involvement of proton transfer to and from the buffer) and there is now coupling between reactions (7) and (2). At the maxima for Tris and tmpy the relaxation time for reaction (7) has become so short that reaction (2) is now rate-limiting; however, the kinetic efficiency of  $\text{NEt}_3$  is so low that this condition is never reached with this buffer. The

**Table 3** Variation<sup>a</sup> in  $\tau^{-1}$  with pH and buffer for the reaction of [Zn(nta)] with 5-nitrosalicylic acid

pH	Buffer	$\tau^{-1}/10^3 \text{ s}^{-1}$	pH	Buffer	$\tau^{-1}/10^3 \text{ s}^{-1}$
9.00	<i>b</i>	26.1	8.62	<i>c</i>	16.7
8.80	<i>b</i>	21.6	8.40	<i>c</i>	14.9
8.60	<i>b</i>	18.7	8.20	<i>c</i>	14.0
8.40	<i>b</i>	16.4	7.90	<i>c</i>	13.0
8.23	<i>b</i>	14.3	9.07	<i>d</i>	18.4
8.01	<i>b</i>	13.6	8.88	<i>d</i>	16.4
9.04	<i>c</i>	22.8	8.68	<i>d</i>	14.4
8.82	<i>c</i>	19.8	8.36	<i>d</i>	13.0

<sup>a</sup> Data refer to 20 °C and  $I = 0.3 \text{ mol dm}^{-3}$  (NaCl). The weighed-in concentration of zinc was  $2.40 \times 10^{-2} \text{ mol dm}^{-3}$ . <sup>b</sup> tmpy: weighed-in concentration  $3.60 \times 10^{-2} \text{ mol dm}^{-3}$ . <sup>c</sup> Tris: weighed-in concentration  $3.60 \times 10^{-2} \text{ mol dm}^{-3}$ . <sup>d</sup> Tris: weighed-in concentration  $9.60 \times 10^{-2} \text{ mol dm}^{-3}$ .



**Fig. 2** Variation of  $\tau^{-1}$  with  $c_{\text{ML}}/[1 + (c_{\text{H}}/K_{\text{Hnsa}})]$  (see text) for the reaction of  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^{-}$  with  $\text{nsa}^{2-}$ . The buffer and ratio of weighed-in buffer:zinc concentrations were: (O) tmpy, 1.5:1.0; (□) Tris, 1.5:1.0; (Δ) Tris, 4.0:1.0

eventual decrease in  $\tau^{-1}$  at high Tris and tmpy concentrations can be attributed to the formation of increasing amounts of  $[\text{Zn}(\text{nta})\text{B}]$  ternary complexes for these two buffers.

Data in the literature for related reactions are consistent with the above interpretation but a complete understanding of the kinetics of the Zn-nta-nsa system evidently requires that reactions (7) and (8) should be quantified. We therefore report the kinetics of reaction (7) in section (iii) and the spectrophotometric determination of the formation constants of buffer ternary complexes using 5-nitrosalicylic acid as an indicator in section (iv).

The variation of  $\tau^{-1}$  with pH at constant weighed-in concentration of zinc is given in Table 3 for three different buffer conditions: Tris and tmpy with a ratio of weighed-in buffer:zinc concentrations of 1.5:1.0, and Tris with a ratio of 4.0:1.0. The rate constants reported in section (iii) indicate that in all three cases there is complete kinetic buffering of reaction (7). Based on the equilibrium constants reported in section (iv), the distribution diagrams show a large variation in the amount of  $[\text{Zn}(\text{nta})\text{B}]$  formed. In terms of the proportion of total nta

present, the latter varies from 0.6 in the 4:1 Tris solution at pH 9 to 0.1 in the tmpy solution at pH 8. Fig. 2 shows a plot of  $\tau^{-1}$  vs.  $c_{ML}/[1 + (c_H/K_{Hnsa})]$  for all three sets of data. The fact that this is a good straight line confirms our analysis, including the assumptions that  $[Zn(nta)(H_2O)_2]^-$  and  $nsa^{2-}$  are the only kinetically active species involved in the formation of  $[Zn(nta)(nsa)]^{3-}$  and that kinetic buffering of reaction (7) has been achieved. The derived rate constants are given in Table 2.

### (iii) Deprotonation of Hnsa<sup>-</sup>

The temperature-jump experiments were carried out with solutions of 5-nitrosalicylic acid of total concentration  $c_{nsa} = ([Hnsa^-] + [nsa^{2-}])$  and buffer of total concentration  $c_B = ([B] + [HB^+])$ , usually under the condition  $c_B \gg c_{nsa}$ . Following the temperature jump a rapid absorbance change attributable<sup>21</sup> to the temperature dependence of the absorption coefficients of nsa species occurred within the heating time of the machine. This was followed by a chemical relaxation in the 10–100  $\mu$ s time range due to proton transfer.

The general reaction scheme for proton transfer between 5-nitrosalicylic acid and buffer species is shown in Scheme 1 where the deprotonated form B of the buffer is assumed to be neutral. It involves<sup>22</sup> a protolytic and a hydrolytic pathway as well as direct exchange, although no more than two of these will be important at a given pH. In the range pH 4–10 a single relaxation effect is to be expected,<sup>22</sup> whose characteristic time is given by equation (9). If use is made of the acid-dissociation constants of  $HB^+$  and  $Hnsa^-$ ,  $K_{HB}$  and  $K_{Hnsa}$  respectively, this can be rewritten<sup>21</sup> in the form (10) where  $k_r$  and  $F$  are defined in expressions (11) and (12).

$$\tau^{-1} = \left[ k_{23} + \frac{k_{21}k_{13}}{k_{12}[nsa^{2-}] + k_{13}[B]} + \frac{k_{24}k_{43}}{k_{42}[HB^+] + k_{43}[Hnsa^-]} \right] ([Hnsa^-] + [B]) + \left[ k_{32} + \frac{k_{31}k_{12}}{k_{12}[nsa^{2-}] + k_{13}[B]} + \frac{k_{34}k_{42}}{k_{42}[HB^+] + k_{43}[Hnsa^-]} \right] ([nsa^{2-}] + [HB^+]) \quad (9)$$

$$\tau^{-1} = k_r F \quad (10)$$

$$k_r = k_{23} + \frac{k_{21}k_{13}}{k_{12}[nsa^{2-}] + k_{13}[B]} + \frac{k_{24}k_{43}}{k_{42}[HB^+] + k_{43}[Hnsa^-]} \quad (11)$$

$$F = [B] + [Hnsa^-] + (K_{HB}/K_{Hnsa})([HB^+] + [nsa^{2-}]) \quad (12)$$

Preliminary experiments with Tris,  $NEt_3$ , tmpy and diethylenetriamine (dien) indicated that direct exchange, [Scheme 1, (2)  $\rightleftharpoons$  (3)], is not the only important reaction path, since plots of  $\tau^{-1}$  vs.  $F$  did not give straight lines passing through the origin. Consideration of the way in which  $1/\tau F (= k_r)$  [equation (10)] varied with the concentrations of the individual reactant species suggested that the additional pathway involved hydrolysis [third term in equation (11)] rather than protolysis (second term) and this was confirmed in the following way.

Although the plots of  $\tau^{-1}$  vs.  $F$  for a given buffer at constant  $c_{nsa}$  do not pass through the origin they are all linear. This is shown in Fig. 3 for tmpy and Tris; similar plots were obtained for dien and  $NEt_3$ . In all cases the critical coefficient ( $r^2$ ) was

0.993 or higher. Two features of these plots are noteworthy: (i) the points obtained with a given buffer at different pH are collinear (shown in Fig. 3 for Tris at pH 9.25 and 8.60), and (ii) the intercept terms are all close to  $0.6 \times 10^4 \text{ s}^{-1}$ . Physically, this intercept term must represent either the deprotonation of  $Hnsa^-$  by  $H_2O$  [Scheme 1, (2)  $\rightarrow$  (1)], or the protonation of  $nsa^{2-}$  by  $H_2O$  [Scheme 1, (3)  $\rightarrow$  (4)], depending on whether the additional pathway referred to above is protolysis or hydrolysis, respectively. Consideration of the individual values rules out the former since the reverse (protonation) rate constant ( $k_{12}$ ) would be considerably higher than the diffusion-

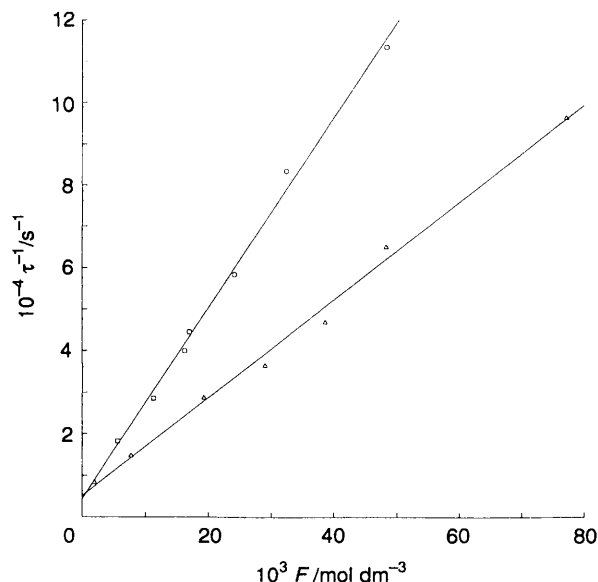
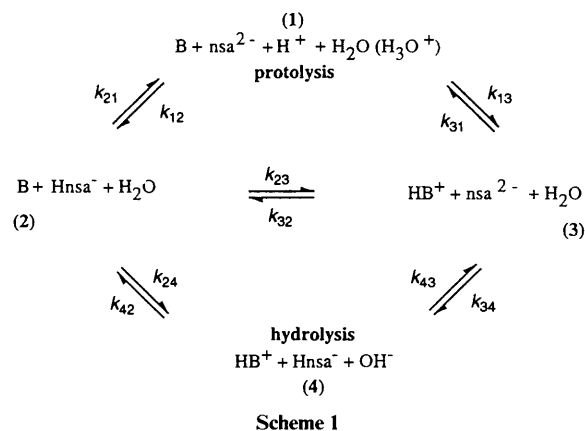


Fig. 3 Variation of  $\tau^{-1}$  with  $F$  (see text) for proton transfer between 5-nitrosalicylic acid and the buffers Tris ( $\circ$ , pH 8.60;  $\square$ , pH 9.25) and tmpy ( $\triangle$ )

Table 4 Rate and equilibrium constants<sup>a</sup> for proton transfer involving 5-nitrosalicylic acid (estimated errors in parentheses):  $Hnsa^- + B \xrightleftharpoons[k_b]{k_a} nsa^{2-} + HB^+$

B	$k_a/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$pK_a(HB^+)$
$NEt_3$	$0.94(0.04) \times 10^6$	$1.3 \times 10^5$	10.80 <sup>b</sup>
dien	$6.81(0.14) \times 10^6$	$3.1 \times 10^7$ <sup>c</sup>	9.94, 9.13 <sup>b</sup>
Tris	$2.30(0.08) \times 10^6$	$1.2 \times 10^8$	8.22 <sup>d</sup>
tmpy	$1.18(0.04) \times 10^6$	$4.1 \times 10^8$	7.40 <sup>d</sup>
$OH^-$	$5.62(0.09) \times 10^7$	$6.2(0.1) \times 10^3$ <sup>e</sup>	6.95 <sup>f</sup>

<sup>a</sup> Data refer to 20 °C and  $I = 0.3 \text{ mol dm}^{-3}$  (NaCl);  $k_a = k_{23}$  for buffers and  $k_{43}$  for  $OH^-$ ;  $k_b = k_{32}$  for buffers and  $k_{34}$  for  $H_2O$ ;  $pK_a(Hnsa^-) = 9.94$  (ref. 16). <sup>b</sup> Ref. 11. <sup>c</sup> Value assumes  $pK_a = 9.28$  (see text). <sup>d</sup> Ref. 23. <sup>e</sup> First-order rate constant ( $s^{-1}$ ). <sup>f</sup> Ref. 12.

controlled value. On the other hand, the values derived on the assumption that the intercept term is  $\{k_{24}k_{43}/(k_{42}[\text{HB}^+] + k_{43}[\text{Hnsa}^-])\}F$  are all in line with expectation for the types of reactants involved (see Discussion).

Table 4 summarizes the acid-dissociation constants assumed for the calculations and the derived rate constants. The values of  $k_a$  for the buffers ( $k_{23}$ ) are the slopes of the  $\tau^{-1}$  vs.  $F$  plots; the values of  $k_b$  have been evaluated using the respective  $pK_a$  values and  $pK_w$ . In the case of dien there are two relevant  $pK_a$  values, 9.94 and 9.13. The values of  $F$  (and therefore the rate constants) have been calculated on the assumption that each protonated or unprotonated amino group is equally effective in its reaction with  $\text{nsa}^{2-}$  or  $\text{Hnsa}^-$ , respectively.

#### (iv) Ternary complexes with the buffer

The UV/VIS spectra<sup>16</sup> of free and complexed  $\text{nsa}^{2-}$  show sharp maxima at 410 and 373 nm, respectively, while that of  $\text{Hnsa}^-$  has a broad maximum centred at about 315 nm. Standard spectrophotometric techniques were used to determine  $K_{\text{MLA}}$ , the stability constant of  $[\text{Zn}(\text{nta})(\text{nsa})]^{3-}$ , employing wavelengths in the ranges 300–320 and 370–410 nm. A value of  $(1.01 \pm 0.11) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  was obtained at 293 K.

Preliminary experiments with solutions containing 5-nitrosalicylic acid mainly in the form of  $\text{Hnsa}^-$  showed that the peak due to  $[\text{Zn}(\text{nta})(\text{nsa})]^{3-}$ , on the edge of the rising  $\text{Hnsa}^-$  absorbance, could be used to monitor the formation of buffer ternary complexes  $[\text{Zn}(\text{nta})\text{B}]$ . Thus, a solution containing suitable concentrations of zinc, nitrilotriacetic acid and 5-nitrosalicylic acid buffered at pH 8.60 with  $\text{NEt}_3$  (which does not form a ternary complex) exhibited a well defined peak at about 375 nm. When either increasing amounts of Tris were added or Tris was used (in increasing concentration) in place of  $\text{NEt}_3$  to maintain the pH the peak at 375 nm was depressed, eventually merging with the edge of the main absorbance to lower wavelength. The buffer ternary stability constants  $K_{\text{MLB}}$  were determined by the following modification of the method of Hague and Eigen.<sup>19</sup>

If  $\Sigma$  is the total concentration of 5-nitrosalicylic acid and  $\epsilon_{\text{MLA},\lambda}$  the molar absorption coefficient of  $[\text{Zn}(\text{nta})(\text{nsa})]^{3-}$  at a given wavelength  $\lambda$  then it may be shown that equation (13)

$$\frac{\sum \epsilon_{\text{MLA},\lambda} = (A_1 - A_2)\{1 + ([\text{H}^+]/K_{\text{Hnsa}})\} + K_{\text{MLA}}(A_1[\text{ML}]_1 - A_2[\text{ML}]_2)}{K_{\text{MLA}}([\text{ML}]_1 - [\text{ML}]_2)} \quad (13)$$

applies. In this equation,  $A_1$  and  $A_2$  are the absorbances of two solutions at the same pH and  $\Sigma$  but different weighed-in concentrations of  $[\text{Zn}(\text{nta})]$ ,  $[\text{ML}]_1$  and  $[\text{ML}]_2$ , respectively (which are  $\gg \Sigma$ ), and  $K_{\text{MLA}}$  is  $[\text{Zn}(\text{nta})(\text{nsa})]/[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2][\text{nsa}^{2-}]$ . Equation (13) was derived on the assumption that no buffer ternary complex  $[\text{Zn}(\text{nta})\text{B}]$  is formed.

If, now,  $\text{NEt}_3$  is replaced by a complexing buffer a suitably rearranged form of equation (13) can be used to determine the concentration of *uncomplexed*  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$  present. Knowing the weighed-in concentrations and  $pK_a$  values of  $[\text{Zn}(\text{nta})]$  and buffer, it is therefore possible to evaluate all the concentration terms in the defining expression for  $K_{\text{MLB}}$ , *i.e.*  $[\text{Zn}(\text{nta})\text{B}]/[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2][\text{B}]$ . For each buffer,  $K_{\text{MLB}}$  was evaluated at five different wavelengths over the range 370–410 nm. The results (293 K) were as follows:  $(6.7 \pm 0.7) \times 10^2$  for imidazole,  $35 \pm 2$  for Tris and  $5.2 \pm 1.3 \text{ dm}^3 \text{ mol}^{-1}$  for tmpy. In view of the high value for imidazole, this buffer was not used in the kinetic experiments with  $\text{nsa}^{2-}$  [section (ii)].

## Discussion

Our objective in the present paper has been to establish the conditions under which reliable kinetics can be determined for

zinc ternary complex formation with bipy and  $\text{nsa}^{2-}$ , using the relatively well characterized zinc–nitrilotriacetate system. A critical feature has been seen to be the choice of buffer for the reaction with  $\text{nsa}^{2-}$ , where it is essential to ensure that proton transfer is not rate-limiting. In this section we will focus first on the proton-transfer reactions involving  $\text{Hnsa}^-$  and  $\text{nsa}^{2-}$ , and compare our results with those which have been published for similar systems. Then the zinc–nta results will be discussed in the context of the patterns found for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ , with particular reference to the electrostatic effect in the  $\text{nsa}^{2-}$  reaction where bound and incoming ligands both carry negative charges.

#### Proton transfer involving $\text{Hnsa}^-$ and $\text{nsa}^{2-}$

The large retarding effect which internal hydrogen bonding can have on the rates of acid–base reactions in water has been recognized for some years.<sup>22,24</sup> In particular, when the phenolic proton in a salicylate-type monoanion is involved in internal hydrogen-bond chelation with one of the carboxylate oxygens the rate constant for its abstraction by a strong base like  $\text{OH}^-$  is well below that for a diffusion-controlled process. Two mechanistic reasons have been advanced for this, involving respectively a two-step process of ring opening followed by proton transfer to the base, and direct attack by base on the bridging proton. Recent results favour<sup>25</sup> the former explanation in most cases.

The measured values of  $k_a$  for deprotonation of the  $\text{Hnsa}^-$  monoanion (Table 4) are well in line with literature values for this type of reaction. For example, our value for  $\text{OH}^-$  ( $k_{43}$ ) of  $5.6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  compares with those<sup>24</sup> of  $5.3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for thiosalicylate (285 K,  $I = 0.1 \text{ mol dm}^{-3}$ ) and  $3.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for *p*-aminosalicylate (298 K,  $I = 1.0 \text{ mol dm}^{-3}$ ). The observation that the rate constants for the analogous reactions with B ( $k_{23}$ ) are all lower than this is also expected,<sup>22,24</sup> as is the fact that the smallest value is found for the buffer with the largest steric requirement near the receiving N atom, triethylamine. Again, comparable results are to be found in the literature, for example<sup>21</sup>  $1.9 \times 10^6$  and  $4.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  respectively for reaction of the 3,5-dinitrosalicylate monoanion with  $\text{NH}_3$  and cacodylate (dimethylarsinate), and  $8.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the thiosalicylate monoanion reacting with  $\text{NH}_3$  (298 K,  $I = 0.3 \text{ mol dm}^{-3}$ ).

The values  $k_b$  for the protonation of  $\text{nsa}^{2-}$  are also in keeping with the literature results<sup>21,22,24</sup> for similar systems. It is interesting that, while the value of  $k_a$  for the most effective kinetic buffer we studied (dien) is only seven times larger than that for the least effective ( $\text{NEt}_3$ ), the spread of values for  $k_b$  covers more than three orders of magnitude. In particular, triethylamine is such a poor kinetic buffer for studying ternary complex formation with 5-nitrosalicylate by the temperature-jump method not because proton abstraction from  $\text{Hnsa}^-$  is too slow but rather because proton donation to  $\text{nsa}^{2-}$  is. This, in turn, reflects the fact that the  $pK_a$  of the donor (10.80) is higher than that of the acceptor (9.94), so the protonation step is energetically disfavoured. For the equilibrium studies, however,  $\text{NEt}_3$  is the best of the four buffers used since it has an adequate buffer capacity in the relevant pH range but also shows no tendency to form a ternary complex.

#### Ternary complex formation involving $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^-$

In our analysis of the kinetic data for all three zinc–nitrilotriacetate systems we have seen that the data are consistent with a scheme in which only the aqua form of the complex reacts with the incoming ligand, bipy, dmbipy or  $\text{nsa}^{2-}$ . Unfortunately, the participation of the hydroxo form or one or more buffer complexes  $[\text{Zn}(\text{nta})\text{B}]$  cannot be ruled out completely. The 5-nitrosalicylic acid results are also subject to proton ambiguity,<sup>18,26</sup> though the concentration

dependence of  $\tau^{-1}$  argues against the reaction of  $\text{Hnsa}^-$  with  $[\text{Zn}(\text{nta})(\text{OH})(\text{H}_2\text{O})]^{2-}$ .

Relatively few rate constants have been reported for the formation of zinc complexes. Our value of 5.92 for  $\log k_f$  for the  $[\text{Zn}(\text{nta})(\text{H}_2\text{O})_2]^- + \text{bipy}$  reaction (Table 2) compares with one of 6.0 obtained by Wilkins and co-workers<sup>27</sup> for the formation of the corresponding 1:1 complex at 25 °C. Our slightly higher value of  $\log k_f$  for ternary complex formation with dmbipy (6.15) is presumably associated with the inductive effect of the ring methyl groups, also reflected in the higher<sup>11</sup>  $\text{p}K_a$  of Hdmbipy<sup>+</sup> (5.32) compared with that of Hbipy<sup>+</sup> (4.44). The value of  $k_f$  for the 1:1 complex with  $\text{nsa}^{2-}$  has not been reported.

With so few comparisons possible, it is clearly premature to attempt a parametrization of the effects of bound ligands on the reactivity of  $\text{Zn}^{2+}$  of the type we have recently produced<sup>4,5</sup> for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . Nonetheless, two aspects of the present results deserve comment. (i) As in the corresponding nickel and cobalt cases, the value of  $k_f$  for the formation of  $[\text{Zn}(\text{nta})(\text{nsa})]^{3-}$  is significantly higher than that for the bipy ternary complex ( $\log k_f = 6.89$  and 5.92, respectively). This demonstrates that the incoming  $\text{nsa}^{2-}$  dianion is attracted to the local positive charge on the metal rather than being repelled by the overall negative charge on the  $[\text{M}(\text{nta})]^-$  complex, and provides further evidence that it is inappropriate<sup>18</sup> to apply the simple Fuoss equation<sup>28</sup> using net charges to reactions of this type. (ii) The rate constants for the formation of the zinc- and cobalt-nta ternary complexes of  $\text{nsa}^{2-}$  ( $\log k_f = 6.89$  and 6.50<sup>18</sup>) and of bipy (5.92 and 5.85<sup>5</sup>) are similar to one another even though zinc(II) complexes are 'inherently' about an order of magnitude more substitution labile than those of cobalt(II). For example, the (logarithmic) water-exchange rate constants for  $\text{Zn}^{2+}$  (aq) and  $\text{Co}^{2+}$  (aq) are<sup>29</sup> 7.4 and 6.5, respectively. The key to this similarity for  $[\text{M}(\text{nta})]^-$  could be that the pyramidal ligand produces a similar degree of distortion away from a strictly octahedral co-ordination, and the reaction profile is effectively controlled by this structure: the ionic radii of the two metals are<sup>30</sup> almost identical ( $r_{\text{Zn}} = 74.0$ ,  $r_{\text{Co}} = 74.5$  pm) and molecular mechanics evidence suggests<sup>31</sup> that the distortion is in the direction of the transition state for water exchange. We will explore further the influence of co-ordination geometry on the reactivity of zinc in some of its polyamine complexes, where the distortion can be<sup>32</sup> large enough to lower the co-ordination number to five.

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