Complexation of Manganese(II) and Zinc(II) Ions with Pyridine, 3-Methylpyridine and 4-Methylpyridine in Dimethylformamide

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Complexation of manganese(II) and zinc(II) ions with pyridine (py), 3-methylpyridine (3Me-py), and 4-methylpyridine (4Me-py) has been investigated by calorimetry in dimethylformamide (dmf) containing 0.1 mol dm^{-3} NEt_4ClO_4 as ionic medium at 25 °C. The formation of $[MnL]^{2+}$, and $[ZnL]^{2+}$ and $[ZnL_2]^{2+}$ (L = py, 3Me-py or 4Me-py) was revealed, and their formation constants, reaction enthalpies and entropies were determined. The stability of the $[ML]^{2+}$ (M = Mn or Zn; L = py, 3Me-py or 4Me-py) complexes in dmf linearly increases with increasing basicity of the pyridine derivatives, *i.e.* a logarithmic plot of the formation constants K_1 of these complexes in dmf against the protonation constants of the ligands in aqueous solution obeyed a linear free-energy relationship. However, a plot of the formation enthalpies and entropies of the complexes against the ligand basicity was not linear, the values for $[M(3Me\text{-}py)]^{2+}$ (M = Mn or Zn) deviating. For both metal ions in dmf, the formation of the 3Me-py complexes is enthalpically less favourable and entropically more favourable than those of py and 4Me-py. Thus, the presence of a methyl group in the 3 position in pyridine results in a larger steric interaction between the ligand and dmf in the first co-ordination sphere of the metal ions than those involving py and 4Me-py.

The complexation of pyridine (py) has been extensively studied in aqueous solution. With first-row bivalent transition-metal ions such as manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II), a series of complexes $[M(py)_n]^{2+}$ (n = 1 or 2 for manganese(II), 1–4 for the others) are formed.[1,2] The effect of substituted pyridine derivatives on complexation in aqueous solution has also been studied since they are suitable for elucidating the correlation between the stability of metal complexes and ligand basicity. For 3- and 4-methylpyridine (3Me- and 4Me-py) derivatives, as well as py, logarithmic plots of the first formation constants of their metal complexes against their protonation constants gave a good linear free-energy relationship.[3–5] On the other hand, the formation constants of copper(II) and cadmium(II) complexes with 2-methylpyridines markedly deviate from this relationship and this has been ascribed to steric hindrance of the methyl group in the 2 position.[6] A similar observation to that in aqueous solution has been made for mixed-ligand complexes of pyridines in non-aqueous solution.[7–12] Although formation constants of metal complexes have usually been employed as a means of discussion, it should be noted that enthalpy–entropy compensation in complexation sometimes leads to a monotonous change in formation constants.[13] Thus, reaction enthalpies and entropies should be determined for the quantitative elucidation of complexation behaviour.

In this work we investigated the complexation of manganese(II) and zinc(II) with py, 3Me-py, and 4Me-py in dimethylformamide (dmf) containing 0.1 mol dm^{-3} NEt_4ClO_4 as ionic medium by precise calorimetry at 25 °C. Enthalpic and entropic evidence is provided that the presence of the methyl group in the 3 position in pyridine results in a larger steric interaction between the ligand and dmf molecules co-ordinated within $[M(3Me\text{-}py)]^{2+}$ (M = Mn or Zn) than those within $[M(py)]^{2+}$ and $[M(4Me\text{-}py)]^{2+}$.

Experimental

Reagents.—All chemicals used were of reagent grade. Manganese(II) and zinc(II) perchlorate dmf solvates were prepared by dissolving the metal(II) perchlorate hydrates in dmf and by repeated evaporation of dmf to remove water, and finally recrystallized once from acetone. The solvates were dried at room temperature in a vacuum oven for a few days. Tetraethylammonium perchlorate was recrystallized once from water and dried at 50 °C in a vacuum oven. Dimethylformamide, pyridine, 3-methyl- and 4-methyl-pyridine were dried for several weeks over 4 A molecular sieves and then distilled under reduced pressure. The reagents were stored over 4 A molecular sieves in a dark bottle. All solutions were prepared and treated in a dry-box under a nitrogen atmosphere.

Measurements.—Calorimetric measurements were carried out by using a fully automatic on-line system,[14] consisting of a twin-type calorimeter (Tokyo Riko, Japan). All test solutions contained 0.1 mol dm^{-3} NEt_4ClO_4 as ionic medium. A manganese(II) or zinc(II) perchlorate dmf solution (40 cm^3) was placed in a stainless-steel vessel, the inside wall of which was coated with Teflon, and was titrated with a 1 mol dm^{-3} pyridine, 3Me-py or 4Me-py solution under a dry nitrogen atmosphere by using an APB-118 autoburette (Kyoto Electronics, Japan). The concentration of metal ions in the initial test solutions was varied over the ranges 10–40 and 5–20 mmol dm^{-3} for manganese(II) and zinc(II), respectively, and the total volume of titrant solutions added was 40 cm^3. The vessel was inserted into an aluminium block thermostatted at 25.0 ± 0.0001 °C in an air-bath. A reverse titration procedure, in which a py, 3Me-py, or 4Me-py dmf solution was titrated with 50 mmol dm^{-3} manganese(II) perchlorate or 20 mmol dm^{-3} zinc(II) perchlorate dmf solution, was also performed. Heats of complexation ranging from 0.2 to 2.0 J at each titration point were measured with a certainty of ±0.02 J and were corrected for the heat of dilution of the titrant, which had been determined in advance by separate experiments and found to be very small.

Data Analysis.—The overall formation of the $[ML_n]^{2+}$ complex (M = Mn or Zn; L = py, 3Me-py or 4Me-py) can be defined as in equations (1) and (2) if the formation of only

$$M^{2+} + nL \rightleftharpoons [ML_n]^{2+} \quad (1)$$

$$\beta_n = [ML_n{}^{2+}]/[M^{2+}][L]^n \quad (2)$$

mononuclear species is assumed. The concentrations of free M^{2+} and L are related to their total concentrations, $c_{M,i}$ and $c_{L,i}$, in a solution i by the mass-balance equations (3) and (4),

$$c_{M,i} = [M^{2+}]_i + \Sigma\beta_n[M^{2+}]_i[L]_i{}^n \quad (3)$$

$$c_{L,i} = [L]_i + \Sigma n\beta_n[M^{2+}]_i[L]_i{}^n \quad (4)$$

respectively. A heat q_i measured at the titration point i is a function of the overall formation constant β_n and the enthalpy $\Delta H^{\ominus}_{\beta n}$ of $[ML_n]^{2+}$ as in equation (5), where V_i denotes the

$$q_i = -(V_i\Sigma\beta_n\Delta H^{\ominus}_{\beta n}[M^{2+}]_i[L]_i{}^n - V_{i-1}\Sigma\beta_n\Delta H^{\ominus}_{\beta n}[M^{2+}]_{i-1}[L]_{i-1}{}^n) \quad (5)$$

volume of the test solution. Formation constants and enthalpies were obtained simultaneously by minimizing the error-square sum $\Sigma(q_{i,\mathrm{obs}} - q_{i,\mathrm{calc}})^2$, by using a non-linear least-squares program MQCAL,[15] according to an algorithm proposed by Marquardt.[16]

Results and Discussion

Calorimetric titration curves obtained in the manganese(II)–py, -3Me-py and -4Me-py systems in dmf are shown in Fig. 1. The heat of complexation q measured at each titration point is normalized with the volume of titrant added δv and the ligand concentration in the titrant $c_{L,\mathrm{tit}}$, and the term $-q/(\delta v c_{L,\mathrm{tit}})$ is plotted against c_L/c_M, where c_L and c_M denote the total concentrations of ligand and manganese(II) ion, respectively, in solution. Fig. 2 depicts calorimetric reverse-titration curves. The calorimetric titration data shown in Figs. 1 and 2 were analysed by assuming the formation of various sets of mononuclear manganese(II) complexes, and values of the Hamilton R factor and the standard deviation of the observed heats σ were compared. Among various sets examined, appreciably small R and σ values were attained for the three systems by considering the formation of $[MnL]^{2+}$ (L = py, 3Me-py or 4Me-py). No significant improvement resulted by considering the additional formation of $[MnL_2]^{2+}$, which suggested that complexes higher than $[MnL]^{2+}$ are hardly formed. The results are given in Table 1. As seen in Figs. 1 and 2, the solid lines calculated by using the constants in Table 1 reproduce well the experimental points.

Similarly, for the zinc(II)–py system in dmf the R and σ values for various sets were compared and the results are listed in Table 2. Set 1 considering the formation of $[Zn(py)]^{2+}$ gave large R and σ values. A significant decrease was achieved by the set 1,2, in which the formation of $[Zn(py)]^{2+}$ and $[Zn(py)_2]^{2+}$ was considered. This set was known as the final choice. For the 3Me- and 4Me-py systems the calorimetric titration data were also best explained in terms of the formation of $[ZnL]^{2+}$ and $[ZnL_2]^{2+}$, as seen in Figs. 3 and 4. The results are summarized in Table 3.

The thermodynamic quantities for the stepwise formation of $[MnL_n]^{2+}$ and $[ZnL_n]^{2+}$ [n = 1 for manganese(II), 1 or 2 for

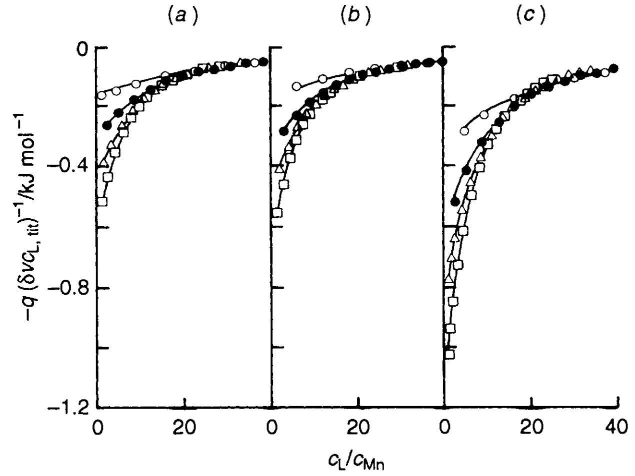

Fig. 1 Calorimetric curves obtained by titrating manganese(II) perchlorate solutions with (*a*) pyridine, (*b*) 3-methylpyridine and (*c*) 4-methylpyridine in dmf. Concentrations of manganese(II) perchlorate, in the initial solutions: (*a*) 10.99 (○), 20.20 (●), 30.08 (△) and 40.84 (□); (*b*) 10.28 (○), 20.42 (●), 29.75 (△) and 41.47 (□); and (*c*) 11.01 (○), 20.24 (●), 30.15 (△) and 40.93 mmol dm^{-3} (□). The solid lines were calculated by using the constants in Table 1

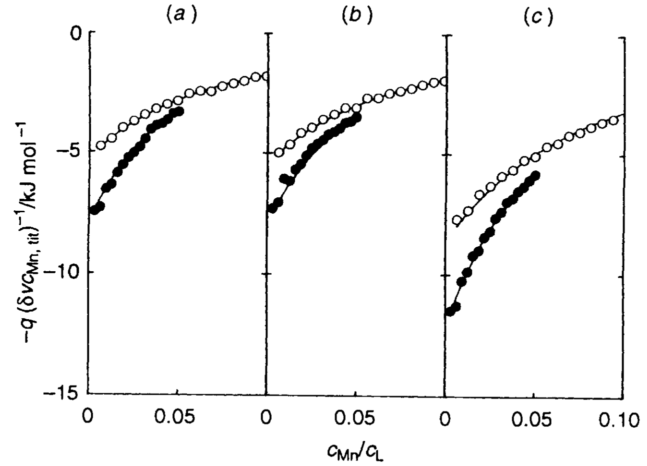

Fig. 2 Calorimetric reverse-titration curves obtained by titrating (*a*) pyridine, (*b*) 3-methylpyridine, and (*c*) 4-methylpyridine solutions with manganese(II) perchlorate in dmf. Concentrations of pyridines in the initial solutions: (*a*) 0.5057 (○) and 1.002 (●); (*b*) 0.5068 (○) and 1.009 (●); and(*c*) 0.5012 (○) and 1.003 (●) mol dm^{-3}. The solid lines were calculated by using the constants in Table 1

Table 1 Results of least-squares refinements of overall formation constants, log(β_n/dm^{3n} mol^{-n}), and enthalpies, $\Delta H^{\ominus}_{\beta n}$/kJ mol^{-1}, of $[MnL_n]^{2+}$ (L = py, 3Me-py or 4Me-py) in dimethylformamide containing 0.1 mol dm^{-3} NEt_4ClO_4 at 25 °C[a]

	py	3Me-py	4Me-py
log β_1	−0.07(3)[a]	0.02(3)	0.13(2)
$\Delta H^{\ominus}_{\beta 1}$	−16.7(7)	−15.1(8)	−20.6(5)
N[b]	89	96	92
R[c]	0.024	0.034	0.019
σ_{obs}[d]/J	0.011	0.016	0.015

[a] The values in parentheses refer to three standard deviations. [b] The number of data points. [c] Hamilton R factor. [d] Standard deviation of the observed heats.

Table 2 Results of least-squares refinements of overall formation constants, log(β_n/dm^{3n} mol^{-n}), and enthalpies, $\Delta H^{\ominus}_{\beta n}$/kJ mol^{-1}, of $[Zn(py)_n]^{2+}$ in dimethylformamide containing 0.1 mol dm^{-3} NEt_4ClO_4 at 25 °C*

	Set 1	Set 1,2
log β_1	0.84(3)	1.06(4)
log β_2	—	0.79 (27)
$\Delta H^{\ominus}_{\beta 1}$	−25.7(7)	−18.1(1.3)
$\Delta H^{\ominus}_{\beta 2}$	—	−41.8(8.1)
R	0.060	0.013
σ_{obs}/J	0.046	0.010

* The number of data points is 104. Values in parentheses refer to three standard deviations.

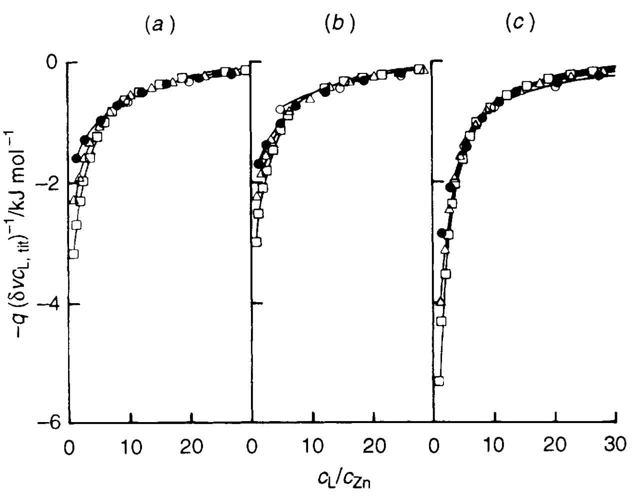

Fig. 3 Calorimetric curves obtained by titrating zinc(II) perchlorate solutions with (*a*) pyridine, (*b*) 3-methylpyridine and (*c*) 4-methylpyridine in dmf. Concentrations of zinc(II) perchlorate in the initial solutions: (*a*) 5.016 (○), 9.286 (●), 14.46 (△) and 21.21 (□); (*b*) 5.056 (○), 10.02 (●), 15.28 (△) and 20.11 (□); and (*c*) 5.016 (○), 9.286 (●), 14.46 (△) and 21.21 mmol dm^{-3} (□). The solid lines were calculated by using the constants in Table 3

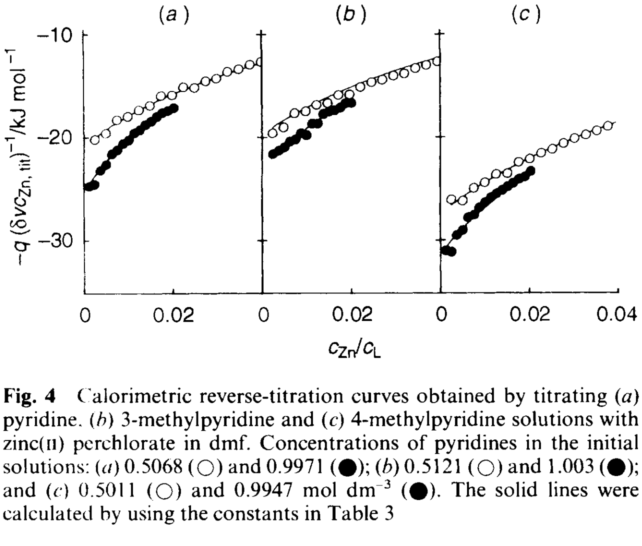

Fig. 4 Calorimetric reverse-titration curves obtained by titrating (*a*) pyridine, (*b*) 3-methylpyridine and (*c*) 4-methylpyridine solutions with zinc(II) perchlorate in dmf. Concentrations of pyridines in the initial solutions: (*a*) 0.5068 (○) and 0.9971 (●); (*b*) 0.5121 (○) and 1.003 (●); and (*c*) 0.5011 (○) and 0.9947 mol dm^{-3} (●). The solid lines were calculated by using the constants in Table 3

Table 3 Results of least-squares refinements of overall formation constants, $\log(\beta_n/\mathrm{dm}^{3n}\ \mathrm{mol}^{-n})$, and enthalpies, $\Delta H^{\circ}_{\beta n}$/kJ mol^{-1}, of $[\mathrm{ZnL}_n]^{2+}$ (L = py, 3Me-py or 4Me-py) in dimethylformamide containing 0.1 mol dm^{-3} $\mathrm{NEt_4ClO_4}$ at 25 °C

	py	3Me-py	4Me-py
$\log \beta_1$	1.06(4)	1.16(10)	1.33(4)
$\log \beta_2$	0.79(27)	1.30(33)	1.57(15)
$\Delta H^{\circ}_{\beta 1}$	−18.1(1.3)	−14.4(2.9)	−20.0(1.4)
$\Delta H^{\circ}_{\beta 2}$	−41.8(8.1)	−30.0(3.0)	−38.4(1.6)
N	104	110	107
R	0.013	0.017	0.015
σ_{obs}/J	0.010	0.017	0.015

zinc(II)] are summarized in Table 4. The species distribution calculated by using the formation constants obtained is shown in Fig. 5.

The manganese(II) and zinc(II) ions are present as hexasolvated $[\mathrm{M(dmf)_6}]^{2+}$ in dmf.[17] Also, the $[\mathrm{ML}]^{2+}$ complexes have a six-co-ordinate structure in dmf since we obtained calorimetric results indicating that $[\mathrm{ML}]^{2+}$ have a six-co-ordinate structure and that a structural change from octahedral to tetrahedral occurs only at a higher step of complexation for the zinc(II) ion in acetonitrile.[18]

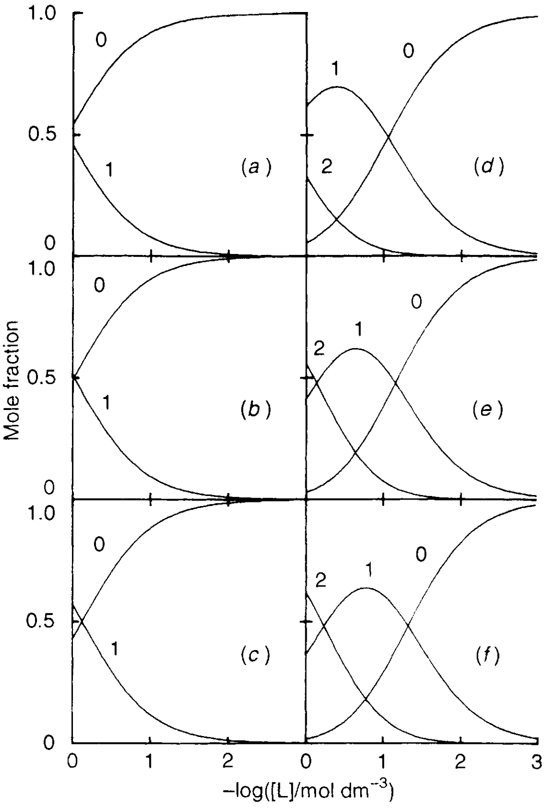

Fig. 5 Distribution of manganese(II) and zinc(II) complexes with pyridines in dmf as a function of −log([L]/mol dm^{-3}); $[\mathrm{ML}_n]^{2+}$ is represented by the *n* value. Systems: (*a*) manganese(II)–py, (*b*) manganese(II)–3Me-py, (*c*) manganese(II)–4Me-py, (*d*) zinc(II)–py, (*e*) zinc(II)–3Me-py and (*f*) zinc(II)–4Me-py

The formation of the $[\mathrm{MnL}]^{2+}$, $[\mathrm{ZnL}]^{2+}$ and $[\mathrm{ZnL_2}]^{2+}$ complexes is exothermic in dmf (see Table 4). The electron-pair donating ability of py (*e.g.*, the donor number $D_{\mathrm{N}} = 33.1$) is greater than that of dmf (26.6).[19] Also, 3Me- and 4Me-py are expected to have higher donor ability than py owing to the substituent effect of the methyl group. Hence, the M–L bonds are thought to be stronger than the M–dmf. The favourable M–L bond formation thus contributes to the exothermic formation of the complexes.

As also seen in Table 4, the entropy changes for the formation of $[\mathrm{MnL}]^{2+}$, $[\mathrm{ZnL}]^{2+}$ and $[\mathrm{ZnL_2}]^{2+}$ are all negative and almost compensate the favourable enthalpy changes. The dmf molecules in the first co-ordination sphere within $[\mathrm{Mn(dmf)_6}]^{2+}$ and $[\mathrm{Zn(dmf)_6}]^{2+}$ are expected to lose freedom of motion to a considerable extent. The solvating dmf molecules are released from the co-ordination sphere upon complexation and then enter a structureless bulk solvent, leading to a large entropy gain as generally seen in aprotic solvents.[20,21] In fact, halogeno complexation of manganese(II) and zinc(II) ions in dmf is accompanied by a large and positive entropy change.[22,23] We suppose that py, 3Me-py and 4Me-py have freedom of motion in bulk dmf because of their weak electron-pair accepting ability, but appreciably lose this freedom upon complexation. Also, since these molecules are bulky, the motion of the dmf molecules within $[\mathrm{MnL}]^{2+}$, $[\mathrm{ZnL}]^{2+}$ and $[\mathrm{ZnL_2}]^{2+}$ is more restricted than that within $[\mathrm{M(dmf)_6}]^{2+}$, owing to the steric interaction between the ligand and dmf molecules in the first co-ordination sphere. These two factors may contribute to the negative entropy changes.

The $[\mathrm{ZnL}]^{2+}$ complex is more stable than the corresponding $[\mathrm{MnL}]^{2+}$ one as expected from the Irving–Williams series (see Fig. 5 and Table 4). Since the enthalpic contribution to

Table 4 Stepwise thermodynamic quantities, $\Delta G_n^{\ominus}$/kJ mol^{-1}, $\Delta H_n^{\ominus}$/kJ mol^{-1} and $\Delta S_n^{\ominus}$/J K^{-1} mol^{-1}, for the formation of $[ML_n]^{2+}$ (M = Mn or Zn; L = py, 3Me-py or 4Me-py) in dimethylformamide containing 0.1 mol dm^{-3} NEt_4ClO_4 at 25 °C

	Mn^{II}			Zn^{II}		
	py	3Me-py	4Me-py	py	3Me-py	4Me-py
$\Delta G_1^{\ominus}$	0.4(2)	−0.1(2)	−0.8(1)	−6.0(2)	−6.6(6)	−7.6(3)
$\Delta G_2^{\ominus}$	—	—	—	2(1)	−1(1)	−1.3(6)
$\Delta H_1^{\ominus}$	−16.7(7)	−15.1(8)	−20.6(5)	−18(1)	−14(2)	−20(1)
$\Delta H_2^{\ominus}$	—	—	—	−24(7)	−16(1)	−18.9(8)
$\Delta S_1^{\ominus}$	−57(3)	−50(3)	−66(2)	−40(5)	−26(10)	−40(6)
$\Delta S_2^{\ominus}$	—	—	—	−85(27)	−50(7)	−59(4)

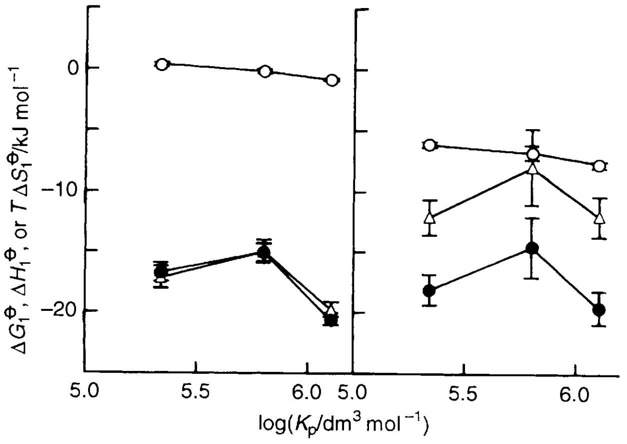

Fig. 6 Plots of $\Delta G_1^{\ominus}$ (○), $\Delta H_1^{\ominus}$ (●) and $T\Delta S_1^{\ominus}$ (△) of the manganese(II) (left) and zinc(II) (right) complexes with pyridines against the ligand basicity. Error bars refer to three standard deviations

the formation of $[ML]^{2+}$ is virtually the same for both manganese(II) and zinc(II), the different stability of the complexes is ascribed to the different entropy change of complexation, *i.e.* the formation of $[ZnL]^{2+}$ is entropically more favourable than that of $[MnL]^{2+}$. The Zn–O (dmf) bond length (208 pm) within $[Zn(dmf)_6]^{2+}$ is shorter than Mn–O (dmf) (216 pm) within $[Mn(dmf)_6]^{2+}$,[17] which suggests that six-co-ordination of the zinc(II) ion is more crowded than that of the manganese(II) ion. The dmf molecules in the first co-ordination sphere within $[Zn(dmf)_6]^{2+}$ are expected to be more restricted than those within $[Mn(dmf)_6]^{2+}$. The solvating dmf molecules around the zinc(II) ion are lost upon complexation to give a larger entropy gain as compared with that of the manganese(II) ion. Also, the motion of the dmf molecules within the $[MnL]^{2+}$ formed is more restricted than that within $[ZnL]^{2+}$ owing to the steric interaction between the ligand and dmf molecules in the first co-ordination sphere, since the dmf molecules around the manganese(II) ion originally have larger entropies than those around the zinc(II) ion.

As seen in Table 4, the stepwise thermodynamic quantities for the formation of the $[ZnL_2]^{2+}$ complexes involve relatively large uncertainties. It is therefore difficult to compare such quantities of the $[ZnL_2]^{2+}$ complexes in detail since the values are not significantly different considering the large uncertainties.

Fig. 6 shows a logarithmic plot of the formation constants K_1 ($\Delta G_1^{\ominus}$) of $[ML]^{2+}$ (M = Mn or Zn) in dmf against the protonation constants K_p of py, 3Me- and 4Me-py in aqueous solution, the values being $10^{5.34}$, $10^{5.80}$ and $10^{6.10}$ dm^3 mol^{-1}, respectively.[1] The stability of the complexes increases with increasing basicity of the nitrogen atoms, *i.e.* the plot obeys a linear free-energy relationship. However, a plot of the formation enthalpies and entropies of the complexes against ligand basicity did not give a linear relationship, since the values for $[M(3Me\text{-}py)]^{2+}$ (M = Mn or Zn) deviated. For both manganese(II) and zinc(II) in dmf, the formation of the 3Me-py complexes is less exothermic and enthalpically less favourable, while the reaction is entropically more favourable than those of the py and 4Me-py complexes. The less exothermic formation is expected to be due to the weaker interaction between the metal(II) ion and 3Me-py compared with py and 4Me-py. This may arise from a weaker M–N bond in $[M(3Me\text{-}py)]^{2+}$ compared to those in $[ML]^{2+}$ (L = py or 4Me-py) and/or weakening of the M–O bond owing to a greater steric interaction of 3Me-py with dmf in the first co-ordination sphere than that of py or 4Me-py. The present study clearly shows that the presence of a methyl group in the 3 position within pyridine results in a larger steric interaction between the ligand and dmf in the first co-ordination sphere of the manganese(II) and zinc(II) ions than that with py and 4Me-py.

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