Thermodynamics of Complexation of Manganese(II) and Zinc(II) Ions with Pyridine, 3-Methyl- and 4-Methyl-pyridine in Cyanomethane

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Complexation of manganese(II) and zinc(II) ions with pyridine (py), 3-methyl- (3Me-py) and 4-methylpyridine (4Me-py) has been investigated by titration calorimetry in cyanomethane (MeCN) containing 0.1 mol dm^{-3} NEt_4ClO_4 as constant ionic medium at 25 °C. The calorimetric titration data are well explained in terms of the formation of $[MnL]^{2+}$, $[MnL_2]^{2+}$ and $[MnL_3]^{2+}$, and $[ZnL]^{2+}$, $[ZnL_2]^{2+}$, $[ZnL_3]^{2+}$ and $[ZnL_4]^{2+}$ (L = py, 3Me-py or 4Me-py), and their formation constants, reaction enthalpies and entropies were determined. In the zinc(II)–py and –4Me-py systems the ΔH°_3 and ΔS°_3 values are large relative to those for other steps, suggesting that an extensive liberation of solvent molecules occurs at the third step. A structural change from octahedral to tetrahedral takes place and octahedral $[ZnL(MeCN)_5]^{2+}$ and $[ZnL_2(MeCN)_4]^{2+}$ and tetrahedral $[ZnL_3(MeCN)]^{2+}$ and $[ZnL_4]^{2+}$ are formed in MeCN. Although an apparent discontinuity in the stepwise thermodynamic parameters is not observed in the zinc(II)–3Me-py system, the overall formation entropy $\Delta S^\circ_{\beta 4}$ indicates a similar structural change. On the other hand, the stepwise thermodynamic quantities for the manganese(II) complexes changed regularly, suggesting an octahedral structure for $[MnL_n(MeCN)_{6-n}]^{2+}$ (n = 1–3). The formation of the manganese(II) and zinc(II) complexes is more favourable in MeCN than in dimethylformamide (dmf), mainly due to the more negative reaction enthalpies in MeCN, resulting from the weaker solvation of the metal ions.

Cyanomethane (MeCN) is an aprotic solvent having a medium relative permittivity (ε = 36.0),[1] which enables it to dissolve electrolytes well, and is widely used in electrochemical measurements as well as dimethylformamide (dmf) having a similar ε value (36.7). Other solvent properties of MeCN and dmf are also similar, *e.g.* dipole moment $\mu_0 = 13.06 \times 10^{-30}$ and 12.86×10^{-30} C m and acceptor number A_N = 19.3 and 16.0 respectively.[1,2] However, their electron-pair donating ability (donor number D_N = 14.1 and 26.6) is different.[2] Nickel(II), copper(II) and zinc(II) ions are more weakly solvated by MeCN than dmf, as indicated by the negative enthalpy of transfer of the ions from MeCN to dmf.[3–5] Metal ions thus have high reactivity in MeCN. Indeed, the chloro complexation of nickel(II), copper(II) and zinc(II) is much more pronounced and proceeds with more negative enthalpies of formation of the complexes in MeCN[3,6,7] than in dmf.[8–10]

We have previously investigated the complexation of manganese(II) and zinc(II) ions with L = pyridine (py), 3-methylpyridine (3Me-py) and 4-methylpyridine (4Me-py) in dmf and elucidated the formation of $[MnL]^{2+}$, $[ZnL]^{2+}$ and $[ZnL_2]^{2+}$.[11] The complexation is exothermic but the negative entropy of the reaction almost compensates the favourable enthalpy change, leading to small formation constants. Entropies associated with the chloro complexation of these metal ions are rather similar in aprotic solvents.[3,6–10,12,13] In order to characterize higher complexes with pyridines such as $[M(py)_3]^{2+}$ and $[M(py)_4]^{2+}$, the complexation should be examined in a solvent having a weaker electron-pair donating ability than that of dmf. The extent of complexation with pyridines should be enhanced in MeCN. Therefore we have now investigated the complexation of manganese(II) and zinc(II) ions with py, 3Me-py and 4Me-py in MeCN containing 0.1 mol dm^{-3} NEt_4ClO_4 as constant ionic medium by precise calorimetry at 25 °C. The thermodynamic parameters in MeCN and dmf are compared and discussed.

Experimental

Reagents.—All chemicals used were of reagent grade. Solutions of manganese(II) and zinc(II) perchlorate in MeCN were prepared by dissolving the metal(II) perchlorate hydrates in MeCN and adding molecular sieves 3A to remove water. The sieves were renewed several times until complete removal of water. The water content in the stock solutions was checked by the Karl-Fischer method to be under 40 ppm. The concentration of metal(II) ions in these solutions was determined by ethylenediamine-*N,N,N′,N′*-tetraacetate titration. Tetraethylammonium perchlorate was recrystallized twice from water and dried at 50 °C in a vacuum oven. Cyanomethane was refluxed over CaH_2 for 1 h to remove water and then distilled under atmospheric pressure. The water content was under 40 ppm. Pyridine, 3Me-py and 4Me-py were dried for several weeks over molecular sieves 4A and then distilled under reduced pressure. The water contents were all under 80 ppm. The reagents were stored over molecular sieves in a dark bottle. All solutions were prepared and treated in a dry-box under a nitrogen atmosphere.

Measurements.—Calorimetric measurements were performed at 25 °C on a twin-type calorimeter (Tokyo Riko, Japan) and a PC-9801VM computer (NEC, Japan) was used for the calorimeter control and data acquisition.[14] Two Teflon-coated stainless-steel vessels were inserted in an aluminium block thermostatted at 25 °C within ±0.0001 °C. All test solutions contained 0.1 mol dm^{-3} NEt_4ClO_4 as constant ionic medium. A manganese(II) or zinc(II) perchlorate solution in MeCN (40 cm^3) was placed in a stainless-steel vessel and titrated with 0.1 mol dm^{-3} pyridine, 3Me-py or 4Me-py solution under a dry nitrogen atmosphere by using an APB-118 autoburet (Kyoto Electronics, Japan). The total volume of titrant solution added was 40 cm^3. The concentration of metal ions in the initial test solutions was varied over the range 5–20 mmol dm^{-3}. Heats of complexation ranging 0.2–2.5 J at each titration point were measured with an error of ±0.02 J (three standard deviations). Heats of dilution of the titrants were separately measured by titrating a 0.1 mol dm^{-3} NEt_4ClO_4 solution in MeCN with the 0.1 mol dm^{-3} ligand solution, and found to be small and used for correction. Heats of dilution of metal-ion solutions were also measured by titrating a similar solution of NEt_4ClO_4 with 10 mmol dm^{-3} metal(II) perchlorate solution. They were also found to be small and thus the heats of dilution of test solutions containing metal(II) perchlorate are negligibly small.

Data Analysis.—If the formation of only mononuclear complexes is assumed, the overall formation of $[ML_n]^{2+}$ ($M = Mn^{2+}$ or Zn^{2+}; L = py, 3Me-py or 4Me-py) can be defined as in equations (1) and (2). The heat q_i evolved at the *i*th titration

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

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

point is expressed as a function of the overall formation constant β_n and the enthalpy $\Delta H^{\ominus}_{\beta n}$ of $[ML_n]^{2+}$ as in equation (3), where V_i denotes the volume of the test solution.

$$q_i = -(V_i\Sigma\beta_n\Delta H^{\ominus}_{\beta n}[M^{2+}]_i[L]^n_i - V_{i-1}\Sigma\beta_n\Delta H^{\ominus}_{\beta n}[M^{2+}]_{i-1}[L]^n_{i-1}) \qquad (3)$$

The concentrations of free M^{2+} and L are related to their total concentrations, $c_{M,i}$ and $c_{L,i}$, in the solution *i* by the mass-balance equations (4) and (5), respectively.

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

$$c_{L,i} = [L]_i + \Sigma n\beta_n[M^{2+}]_i[L]^n_i \qquad (5)$$

Formation constants and enthalpies were simultaneously obtained by minimizing the error-square sum $\Sigma(q_{i,obs} - q_{i,calc})^2$, by using the 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 MeCN are shown in Fig. 1. The term $-q/(\delta v c_{L,tit})$ is plotted where *q* is the heat of complexation measured, δv the volume of titrant added, and $c_{L,tit}$ the concentration of the ligand in the titrant. The calorimetric titration data were analysed by assuming the formation of a set of mononuclear complexes, and values of the Hamilton *R* factor and the standard deviation, σ, of the observed heats were compared for various sets. The results for the manganese(II)–pyridine complexes are listed in Table 1. Set 1,2 encompassing the formation of $[Mn(py)]^{2+}$ and $[Mn(py)_2]^{2+}$ gave large *R* and σ values and failed to reproduce the experimental values. A significant decrease in *R* and σ was achieved by the set 1,2,3 involving the formation of $[Mn(py)]^{2+}$, $[Mn(py)_2]^{2+}$ and $[Mn(py)_3]^{2+}$. No significant improvement in *R* and σ resulted for the set 1,2,3,4 assuming the formation of $[Mn(py)_4]^{2+}$ in addition to the set 1,2,3. Furthermore, log β_3 and log β_4 as well as $\Delta H^{\ominus}_{\beta 3}$ and $\Delta H^{\ominus}_{\beta 4}$ for the set 1,2,3,4 have large uncertainties, indicating a low formation constant for $[Mn(py)_4]^{2+}$. The highest concentration of $[Mn(py)_4]^{2+}$ based on the formation constants for the set 1,2,3,4 is 3–6% at the highest pyridine concentration under the experimental conditions examined, which is not within the limit of detection. It is thus concluded that $[Mn(py)]^{2+}$, $[Mn(py)_2]^{2+}$ and $[Mn(py)_3]^{2+}$ complexes are formed in MeCN. For the 3Me-py and 4Me-py systems the calorimetric data were also explained in terms of the formation of $[MnL]^{2+}$, $[MnL_2]^{2+}$ and $[MnL_3]^{2+}$, the results being listed in Table 2. As seen in Fig. 1, the solid lines calculated by using the constants in Table 2 reproduce well the experimental points over the whole range of c_L/c_M examined.

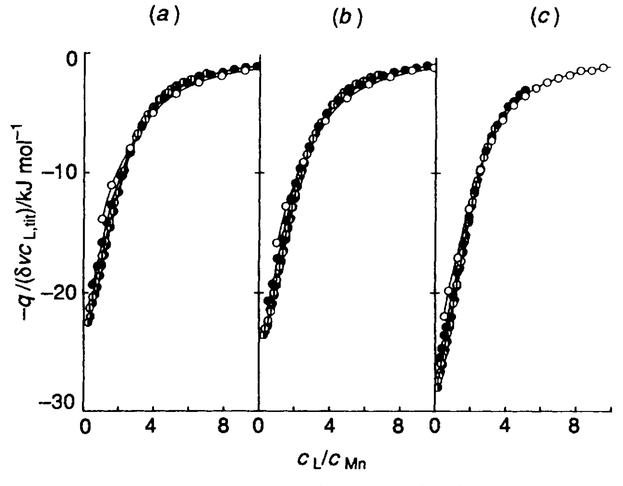

Fig. 1 Calorimetric curves obtained by titrating manganese(II) perchlorate solutions with (*a*) py, (*b*) 3Me-py and (*c*) 4Me-py in MeCN. Concentrations of manganese(II) perchlorate, $c_{Mn,init}$/mmol dm^{-3}, in the initial solutions: (*a*) 5.039 (○), 10.04 (●), 15.16 (⦶) and 20.03 (◑); (*b*) 5.160 (○), 10.04 (●), 15.20 (⦶) and 20.12 (◑); and (*c*) 5.039 (○), 10.04 (●), 15.16 (⦶) and 20.03 (◑). The solid lines were calculated by using the constants in Table 2

Similarly, for the zinc(II) systems in MeCN, the *R* and σ values for various sets were compared and it was revealed that the calorimetric titration data were best explained in terms of the formation of $[ZnL]^{2+}$, $[ZnL_2]^{2+}$, $[ZnL_3]^{2+}$ and $[ZnL_4]^{2+}$, as seen in Fig. 2. The results are given in Table 3.

The thermodynamic quantities for the stepwise formation of $[ML_n]^{2+}$ [*n* = 1–3 for manganese(II), 1–4 for zinc(II)] are

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}, for $[Mn(py)_n]^{2+}$ in cyanomethane containing 0.1 mol dm^{-3} NEt_4ClO_4 at 25 °C[a]

	Set 1,2	Set 1, 2, 3	Set 1, 2, 3, 4
log β_1	2.6 (0.1)[b]	2.74 (0.06)	2.74 (0.07)
log β_2	4.1 (0.1)	4.73 (0.09)	4.76 (0.09)
log β_3	—	5.9 (0.1)	5.8 (0.4)
log β_4	—	—	6.9 (0.6)
$\Delta H^{\ominus}_{\beta 1}$	−25 (2)	−25.3 (0.6)	−25.3 (0.8)
$\Delta H^{\ominus}_{\beta 2}$	−79 (3)	−49 (2)	−48 (2)
$\Delta H^{\ominus}_{\beta 3}$	—	−83 (4)	−87 (34)
$\Delta H^{\ominus}_{\beta 4}$	—	—	−59 (18)
R[c]	0.028	0.009	0.009
σ_{obs}[d]/J	0.043	0.014	0.014

[a] The number of data points is 78. [b] Values in parentheses refer to three standard deviations. [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}, for $[MnL_n]^{2+}$ (L = py, 3Me-py or 4Me-py) in cyanomethane containing 0.1 mol dm^{-3} NEt_4ClO_4 at 25 °C

	py	3Me-py	4Me-py
log β_1	2.74 (0.06)[a]	2.9 (0.1)	2.95 (0.07)
log β_2	4.73 (0.09)	5.1 (0.1)	5.28 (0.09)
log β_3	5.9 (0.1)	6.4 (0.2)	6.9 (0.2)
$\Delta H^{\ominus}_{\beta 1}$	−25.3 (0.6)	−25.8 (0.9)	−30.3 (0.7)
$\Delta H^{\ominus}_{\beta 2}$	−49 (2)	−48 (2)	−52 (1)
$\Delta H^{\ominus}_{\beta 3}$	−83 (4)	−79 (4)	−83 (6)
N[b]	78	89	73
R	0.009	0.015	0.008
σ_{obs}/J	0.014	0.021	0.012

[a] Values in parentheses refer to three standard deviations. [b] The number of data points.

summarized in Table 4. The species distribution calculated by using the formation constants obtained is shown in Fig. 3.

It is most plausible that the manganese(II) and zinc(II) ions exist as hexasolvates $[M(MeCN)_6]^{2+}$ in MeCN.[17] Ligating solvent molecules can be successively replaced with pyridines. A structural change from an octahedral to a tetrahedral geometry around the metal ion sometimes occurs at a certain step of complexation, as found in the case of chloro complexation of nickel(II), copper(II) and zinc(II) ions in MeCN.[3,6,7] Since the structural change is accompanied by an extensive liberation of solvent molecules, an irregular variation of thermodynamic parameters is expected. Less negative enthalpy and entropy values observed at the third step for the zinc(II)–py and -4Me-py systems (see Table 4) indicate that reaction (6) takes place.

$$[ZnL_2(MeCN)_4]^{2+} + L \longrightarrow [ZnL_3(MeCN)]^{2+} + 3MeCN \quad (6)$$

Although an irregular variation of the stepwise thermodynamic parameters is not observed for the zinc(II)–3Me-py system, a structural change from octahedral to tetrahedral should occur because the overall formation enthalpy $\Delta H^{\ominus}_{\beta4}$ and entropy $\Delta S^{\ominus}_{\beta4}$ for this are very similar to those for the py and 4Me-py systems, where $[ZnL_4]^{2+}$ (L = py or 4Me-py) has a tetrahedral structure. Also, the $\Delta S^{\ominus}_2$ value is less negative for the 3Me-py system than for py and 4Me-py, suggesting that more than one co-ordinating MeCN molecule is liberated upon complexation. Thus, we propose the octahedral–tetrahedral equilibrium (7) for $[Zn(3Me\text{-}py)_2]^{2+}$.

$$[Zn(3Me\text{-}py)_2(MeCN)_4]^{2+} \rightleftharpoons [Zn(3Me\text{-}py)_2(MeCN)_2]^{2+} + 2MeCN \quad (7)$$

The stepwise thermodynamic parameters for the complexation of manganese(II) ion with py, 3Me-py and 4Me-py change regularly and the $\Delta S^{\ominus}_{\beta3}$ values are much more negative for manganese(II) than for zinc(II). Thus, no extensive desolvation occurs at any step of complexation, *i.e.* the structure of all the complexes is six-co-ordinate octahedral. This is consistent with our recent result that the manganese(II) ion has an octahedral structure in neat 3Me- and 4Me-py, while zinc(II) has a tetrahedral structure in neat 4Me-py.[18]

The zinc(II) complexes are all more stable than the manganese(II) ones in MeCN, as is seen in Table 4. Since the

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

	py	3Me-py	4Me-py
$\log \beta_1$	3.9 (0.2)*	4.6 (0.4)	3.9 (0.3)
$\log \beta_2$	7.0 (0.2)	8.1 (0.5)	7.3 (0.6)
$\log \beta_3$	9.3 (0.3)	10.6 (0.6)	10.3 (0.7)
$\log \beta_4$	10.6 (0.3)	12.1 (0.7)	12.2 (0.8)
$\Delta H^{\ominus}_{\beta1}$	−32.3 (0.5)	−31.4 (0.7)	−36 (1)
$\Delta H^{\ominus}_{\beta2}$	−61 (1)	−56 (1)	−66 (5)
$\Delta H^{\ominus}_{\beta3}$	−76 (2)	−74 (2)	−72 (3)
$\Delta H^{\ominus}_{\beta4}$	−97 (2)	−90 (2)	−89 (5)
N	67	95	66
R	0.007	0.013	0.012
σ_{obs}/J	0.013	0.024	0.019

* Values in parentheses refer to three standard deviations.

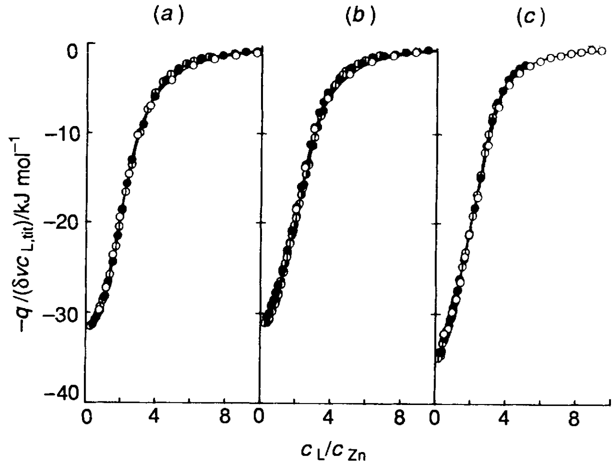

Fig. 2 Calorimetric curves obtained by titrating zinc(II) perchlorate solutions with (*a*) py, (*b*) 3Me-py and (*c*) 4Me-py in MeCN. Concentrations of zinc(II) perchlorate, $c_{Zn,init}$/mmol dm^{-3}, in the initial solutions: (*a*) 5.425 (○), 10.14 (●) and 15.11 (◐); (*b*) 5.070 (○), 10.07 (●), 15.16 (◐) and 20.01 (◑); and (*c*) 5.425 (○), 10.14 (●) and 15.11 (◐). The solid lines were calculated by using the constants in Table 3

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

	Mn^{II}			Zn^{II}		
	py	3Me-py	4Me-py	py	3Me-py	4Me-py
$\Delta G^{\ominus}_1$	−15.6 (0.4)	−16.7 (0.6)	−16.8 (0.4)	−22.1 (0.9)	−26 (2)	−22 (2)
$\Delta G^{\ominus}_2$	−11.4 (0.3)	−12.3 (0.5)	−13.4 (0.3)	−17.9 (0.5)	−20 (1)	−19 (1)
$\Delta G^{\ominus}_3$	−6.4 (0.5)	−7.5 (0.5)	−9.1 (0.6)	−13.2 (0.5)	−14.5 (0.7)	−17 (1)
$\Delta G^{\ominus}_4$	—	—	—	−7.6 (0.7)	−8.3 (0.7)	−11 (2)
$\Delta H^{\ominus}_1$	−25.3 (0.7)	−25.8 (0.9)	−30.3 (0.7)	−32.4 (0.5)	−31.4 (0.7)	−35.6 (0.9)
$\Delta H^{\ominus}_2$	−23 (2)	−22 (3)	−21 (2)	−28 (1)	−24 (1)	−30 (5)
$\Delta H^{\ominus}_3$	−34 (5)	−31 (4)	−31 (6)	−15 (3)	−18 (2)	−7 (7)
$\Delta H^{\ominus}_4$	—	—	—	−21 (2)	−16 (3)	−17 (4)
$\Delta S^{\ominus}_1$	−32 (3)	−31 (5)	−45 (3)	−34 (5)	−18 (9)	−45 (8)
$\Delta S^{\ominus}_2$	−40 (8)	−33 (10)	−26 (7)	−35 (5)	−14 (7)	−36 (20)
$\Delta S^{\ominus}_3$	−93 (17)	−79 (16)	−74 (23)	−8 (10)	−12 (10)	35 (24)
$\Delta S^{\ominus}_4$	—	—	—	−44 (8)	−27 (10)	−21 (16)
$\Delta G^{\ominus}_{\beta3}$[b]	−33.4 (0.8)	−36 (1)	−39.3 (0.8)	−53 (2)	−61 (3)	−59 (4)
$\Delta H^{\ominus}_{\beta3}$[b]	−83 (4)	−79 (4)	−83 (6)	−76 (2)	−74 (2)	−72 (3)
$\Delta S^{\ominus}_{\beta3}$[b]	−165 (16)	−144 (14)	−146 (21)	−77 (9)	−43 (15)	−45 (17)
$\Delta G^{\ominus}_{\beta4}$[c]	—	—	—	−61 (2)	−69 (4)	−69 (5)
$\Delta H^{\ominus}_{\beta4}$[c]	—	—	—	−97 (2)	−90 (2)	−89 (5)
$\Delta S^{\ominus}_{\beta4}$[c]	—	—	—	−121 (12)	−70 (17)	−66 (26)

[a] Values in parentheses refer to three standard deviations. [b] The overall formation of $[ML_3]^{2+}$. [c] The overall formation of $[ML_4]^{2+}$.

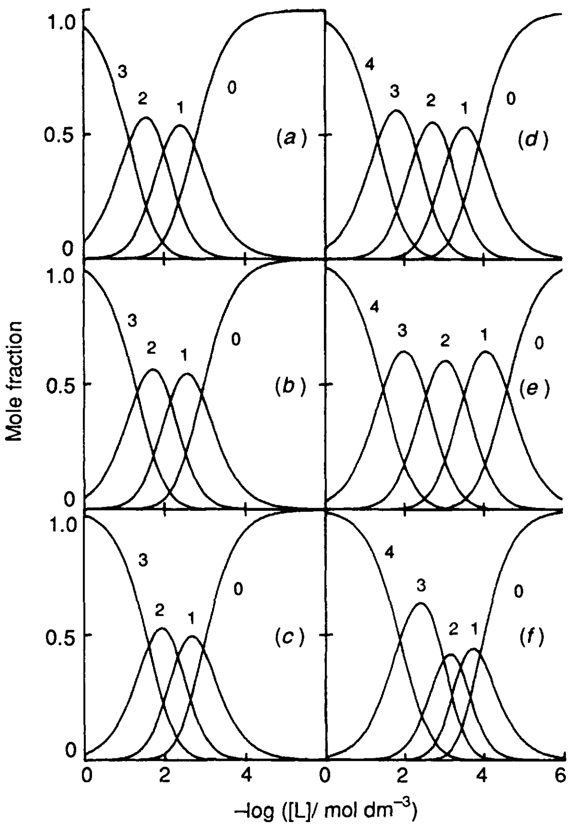

Fig. 3 Species distribution for manganese(II) and zinc(II) with pyridines in MeCN as a function of $-\log([L]/\text{mol dm}^{-3})$; $[ML_n]^{2+}$ is represented by the *n* value (0–4): (*a*) manganese(II)–py, (*b*) manganese(II)–3Me-py, (*c*) manganese(II)–4Me-py, (*d*) zinc(II)–py, (*e*) zinc(II)–3Me-py and (*f*) zinc(II)–4Me-py

structure of $[MnL_2]^{2+}$ and $[MnL_3]^{2+}$ is different from that of $[ZnL_2]^{2+}$ and $[ZnL_3]^{2+}$, the desolvation is different in the manganese(II) and zinc(II) systems. It is therefore difficult to compare directly the stepwise thermodynamic parameters for the formation of $[ML_2]^{2+}$ and $[ML_3]^{2+}$ (M = Mn or Zn). The pronounced stability of $[ZnL]^{2+}$ compared with $[MnL]^{2+}$ in MeCN originates from the enthalpic term because the entropy is virtually the same for the two complexes within experimental uncertainties. This is due to the larger affinity of nitrogen atom for zinc(II) ion compared with manganese(II) ion, *i.e.* more negative enthalpy changes are usually observed for complexation of zinc(II) than for manganese(II) with nitrogen donors.[19,20]

Fig. 4 shows plots of the $\Delta G^\ominus_1$, $\Delta H^\ominus_1$ and $\Delta S^\ominus_1$ values for the manganese(II) and zinc(II) complexes in MeCN against the logarithmic value of the protonation constants $\log(K_p/\text{dm}^3\ \text{mol}^{-1})$ of py, 3Me-py and 4Me-py in aqueous solution,[19] together with those in dmf.[11] The formation of octahedral $[ML]^{2+}$ (M = Mn or Zn; L = py, 3Me-py, 4Me-py) is more favourable in MeCN than in dmf. The difference in the stability of the complexes in MeCN and in dmf is predominantly due to the enthalpic difference. Consistent with the weaker electron-pair donating ability of MeCN than that of dmf as well as the endothermicity in the transfer of the zinc(II) ion from dmf to MeCN,[2,5] the manganese(II) and zinc(II) ions are more weakly solvated in MeCN than in dmf. Less energy is thus needed for breaking the M–MeCN bond, resulting in more exothermic complexation in MeCN than in dmf. Reaction entropies for the chloro complexation of nickel(II), copper(II) and zinc(II) ions are similar in MeCN and in dmf or even smaller in MeCN than in dmf,[3,6–10] *i.e.* the chloro complexation is not entropically favourable in MeCN over that in dmf. On the other hand, entropies for the formation of $[ZnL]^{2+}$ are similar in MeCN and in dmf and those for $[MnL]^{2+}$ are even larger in MeCN than in dmf, *i.e.* the formation of $[ML]^{2+}$ is entropically favourable in MeCN compared with dmf. Also, entropies for the formation of $[ML]^{2+}$ are largely negative. Pyridines are bulky and the motion of the solvent molecules within $[ML(solv)_5]^{2+}$ (solv = MeCN or dmf) is more restricted than that within $[M(solv)_6]^{2+}$. However, the linear structure of the MeCN molecule is expected to reduce the restriction of the MeCN molecules within $[ML(MeCN)_5]^{2+}$. This is especially so for manganese(II) having a larger ionic radius than that of zinc(II),[21] leading to the larger entropy for the formation of $[MnL]^{2+}$ in MeCN than in dmf.

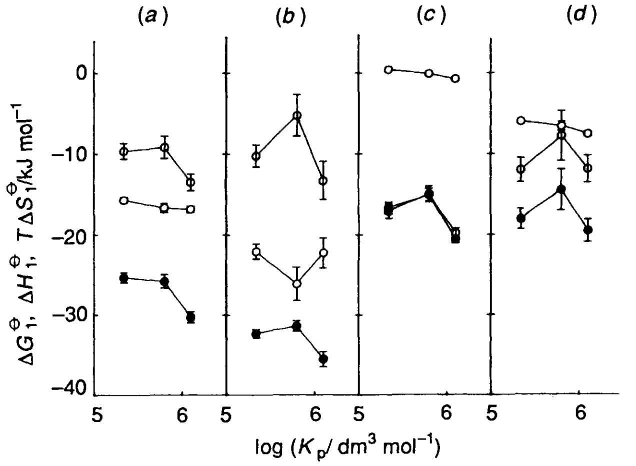

Fig. 4 Plots of the $\Delta G^\ominus_1$(○), $\Delta H^\ominus_1$ (●) and $T\Delta S^\ominus_1$ (◐) values for complexation of pyridines with (*a*) manganese(II) and (*b*) zinc(II) in MeCN and (*c*) manganese(II) and (*d*) zinc(II) in dmf against the basicity of the ligands. Error bars refer to three standard deviations

The ion $[ZnL]^{2+}$ is more stable than $[MnL]^{2+}$ in both MeCN and dmf. While this difference is due to the difference in the entropy values in dmf, it has an enthalpy origin in MeCN. In dmf, the Zn–O (dmf) bond length (208 pm) within $[Zn(dmf)_6]^{2+}$ is shorter than Mn–O (dmf) (221 pm) within $[Mn(dmf)_6]^{2+}$,[22,23] which suggests zinc(II) has the more crowded six-co-ordination. Rotation around the M–O bond is more restricted within $[Zn(dmf)_6]^{2+}$ than within $[Mn(dmf)_6]^{2+}$, because of the planar structure of dmf. Thus, the dmf molecules around the manganese(II) ion originally have larger entropies than those around the zinc(II) ion. Owing to the large steric interaction among the ligand and dmf molecules in the first co-ordination sphere, the motion of the dmf molecules within the $[MnL]^{2+}$ formed is then more restricted than that within $[ZnL]^{2+}$, leading to the smaller entropy for manganese(II) in dmf. On the other hand, MeCN is a linear molecule and the extent of rotation around the M–N bond, *i.e.* the freedom of motion of the solvating molecules, is similar for the solvated zinc(II) and manganese(II) ions. Also, the steric interaction between the MeCN and pyridines in the first co-ordination sphere is expected to be similar for the manganese(II) and zinc(II) complexes. This is reflected in the similar entropic change for complexation of the two metal ions in MeCN.

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