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Complexation of Zinc(II) and Cadmium(II) by Hydroxyethyl- and Bis(hydroxyethyl)-1,4,7-triazacyclononane in Water

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The complexation of Zn^{2+} by hydroxyethyl- and bis(hydroxyethyl)-1,4,7-triazacyclononane ((2) and (3)) in aqueous solution at 298.2 K and $I = 0.10$ mol dm^{-3} ($NaNO_3$) is characterized by $\log(K/\text{dm}^3\,\text{mol}^{-1}) = 10.45 \pm 0.05$ and 11.32 ± 0.02 and a deprotonation assigned to coordinated water is characterized by $pK_a = 8.87 \pm 0.11$ and 8.50 ± 0.03, respectively. For the analogous Cd^{2+} complexes $\log(K/\text{dm}^3\,\text{mol}^{-1}) = 8.74 \pm 0.02$ and 9.79 ± 0.02, respectively, and no deprotonation of coordinated water is detected. The synthesis of (2) is described.

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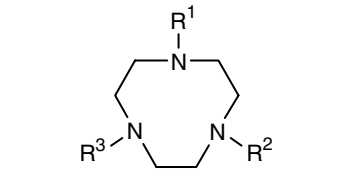
Introduction

1,4,7-Triazacyclononane, (1) in Scheme 1, has been the subject of several metal complexation studies[1–4] as have its homo trisubstituted derivatives.[5–12] The robustness of (1) makes it an attractive platform for controlled sequential substitution at each of the secondary amines as exemplified by hydroxyethyl-, bis(hydroxyethyl)-, and tris(hydroxyethyl)-1,4,7-triazacyclononane ((2), (3), and (4), respectively). As this sequential substitution proceeds there is an interplay between the changing basicity of the amine nitrogens and increasing ligand denticity, which is here explored through the protonation of ligands (2) and (3) and their complexation of Zn^{2+} and Cd^{2+}, and a comparison with their unsubstituted and fully substituted analogues, (1) and (4), respectively.

Results and Discussion

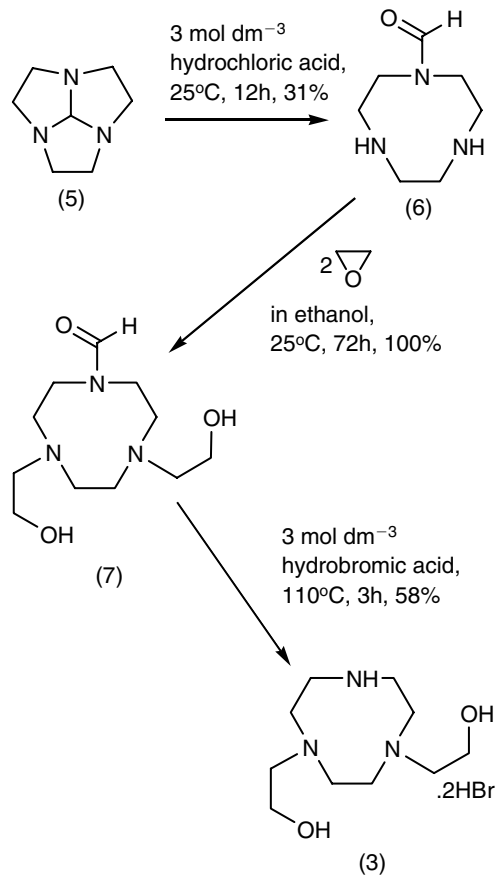
Ligand Syntheses

Syntheses of the mono- and bis-substituted derivatives of (1) proceed through the bridged macrocycle 1,4,7-triazatricyclo[5.2.1.0$^{4.10}$]decane, (5), as shown for (3).2 HBr in Scheme 2. (We earlier described the synthesis of (2).2 HBr.[13]) This synthesis, an adaptation of a literature method for the syntheses of bis-*N*-substituted 1,4,7-triazacyclononanes,[15] commenced with stirring 1,4,7-triazatricyclo[5.2.1.0$^{4.10}$]decane, (5), in 3 mol dm^{-3} hydrochloric



(1); $R^1 = R^2 = R^3 = H$
(2); $R^1 = R^2 = H$, $R^3 = CH_2CH_2OH$
(3); $R^1 = H$, $R^2 = R^3 = CH_2CH_2OH$
(4); $R^1 = R^2 = R^3 = CH_2CH_2OH$

Scheme 1.



Scheme 2.

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acid at 25°C for 12 h, adjusting the pH to 9 and extracting 1-formyl-1,4,7-triazacyclononane, (6), into dichloromethane. The reaction of (6) with ethylene oxide in ethanol at 25°C for 72 h gave 1-formyl-4,7-bis(2-hydroxyethyl)-1,4,7-trazacyclononane, (7), as a viscous oil, which was refluxed at 110°C for 3 h in 3 mol dm^{-3} hydrobromic acid to give 1,4-bis(2-hydroxyethyl)-1,4,7-triazacyclononane dihydrobromide, (3).2 HBr, as white needles.

In a second method two equivalents of sodium ethoxide were added to 1,4,7-triazacyclononane trihydrobromide, (1).3 HBr, in dry ethanol, followed by reaction with two equivalents of ethylene oxide for 72 h at 25°C. The resulting viscous oil was treated with 6 mol dm^{-3} hydrobromic acid and recrystallized from ethanol to give (3).2 HBr as white needles. However, this method can give difficult to separate mixtures of (2).2 HBr and (3).2 HBr.

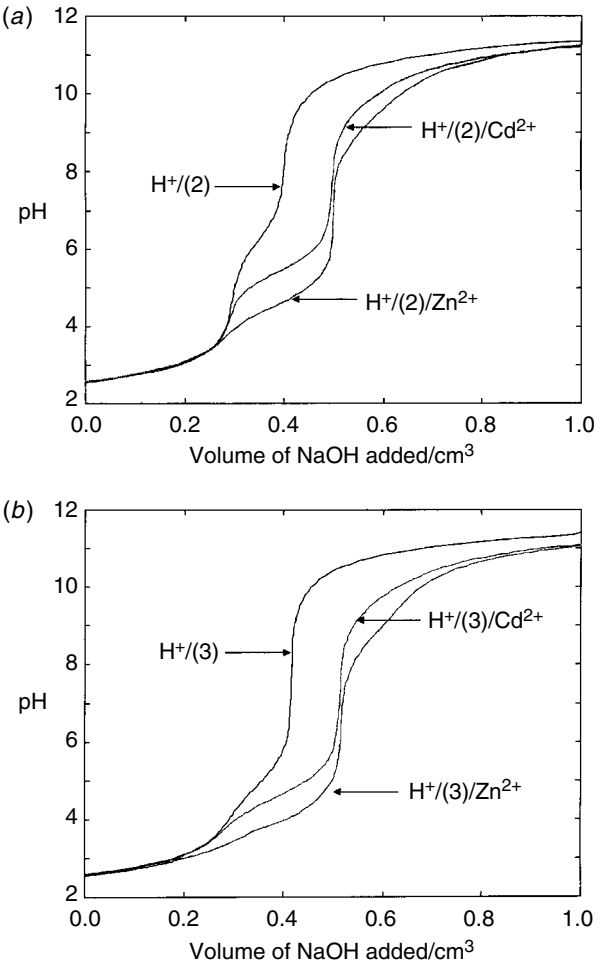

Fig. 1. (*a*) Typical titration curves at 298.2 K for a solution of 0.005 mol dm^{-3} HNO_3 and 0.001 mol dm^{-3} (2); a solution of 0.005 mol dm^{-3} $HClO_4$, 0.001 mol dm^{-3} (2), and 0.001 mol dm^{-3} $ZnSO_4$; and a solution of 0.005 mol dm^{-3} HNO_3, 0.001 mol dm^{-3} (2), and 0.001 mol dm^{-3} $CdSO_4$ as annotated. (*b*) Typical titration curves at 298.2 K for a solution of 0.005 mol dm^{-3} HNO_3 and 0.001 mol dm^{-3} (3); a solution of 0.005 mol dm^{-3} HNO_3, 0.001 mol dm^{-3} (3), and 0.001 mol dm^{-3} $ZnSO_4$; and a solution of 0.005 mol dm^{-3} HNO_3, 0.001 mol dm^{-3} (3), and 0.001 mol dm^{-3} $CdSO_4$ as annotated. The titrant was 0.100 mol dm^{-3} NaOH. For all titration solutions I = 0.10 mol dm^{-3} ($NaNO_3$).

*Potentiometric Determination of the p*K$_a$*s of (2).H_3^{3+} and (3).H_3^{3+}*

The titration of (2).H_3^{3+} and (3).H_3^{3+} with NaOH results in titration curves (Fig. 1) characterizing three acid dissociations whose pK_a values appear in Table 1 together with those of (1).H_2^{2+} and (4).H_2^{2+}.[2,5] The pK_{a1} values vary in the sequence (1).H^+ > (2).H^+ < (3).H^+ < (4).H^+ within an order of magnitude variation in acidity, suggesting that the lowering of amine nitrogen basicity caused by the electron withdrawing effect of a single hydroxyethyl pendant arm in (2).H^+ is offset by a compensating effect in (3).H^+ and (4).H^+. It is probable that protonation in (1).H^+ is stabilized through hydrogen bonding with secondary amine groups, while (2).H^+ is less stable because its tertiary amine is less basic, and the extent of intra-amine hydrogen bonding is correspondingly decreased. This decrease in intra-amine hydrogen bonding is likely to further decrease in (3).H^+ and (4).H^+ as the number of hydroxyethyl pendant arms increases but intramolecular hydrogen bonding of the protonated amine and the hydroxy groups of the pendant arms becomes increasingly possible. This appears to offset the decreased basicity of the tertiary amine nitrogens and be the origin of the increase in the pK_{a1} values of (3).H^+ and (4).H^+. The much lower pK_{a1} (Table 1) of the more flexible (8).H^+ linear analogue of (1).H^+, where (8) is linear diethylenetriamine, suggests that the relatively rigid macrocyclic structures of (1)–(4) greatly increases their basicity, so that (1).H^+–(4).H^+ are substantially less acidic because of the greater extent of intramolecular hydrogen bonding.[16]

The pK_{a2} values are smaller because of intra-protonic charge repulsion. There is also a systematic decrease in magnitude from (1).H_2^{2+} to (4).H_2^{2+} corresponding to a change of greater than three orders of magnitude in acidity which is consistent with a decreasing effectiveness of intramolecular hydrogen bonding with an increase in pendant arm substitution. However, the increase in pK_{a1} relative to pK_{a2} for

Table 1. Acid dissociation constants and complexation constants for Zn^{2+} and Cd^{2+} complexes in aqueous solution at 298.2 K and I = 0.10 mol dm^{-3} ($NaNO_3$)[A]

Ligand	pK_{a1}	pK_{a2}	pK_{a3}
(1).H_3^{3+}	10.42[B]	6.82[B]	–
(2).H_3^{3+}	10.24 ± 0.02[C]	6.17 ± 0.02[C]	1.97 ± 0.05[C]
(3).H_3^{3+}	11.02 ± 0.05[C]	4.97 ± 0.07[C]	2.25 ± 0.14[C]
(4).H_3^{3+}	11.50 ± 0.01[C] 11.52[D]	3.97 ± 0.06[C] 3.42[D]	–
(8).H_3^{3+}	9.84[E]	9.02[E]	4.23[E]

	log(K_{Zn}/dm^3 mol^{-1})	log(K_{Cd}/dm^3 mol^{-1})	pK_{aZn}
(1)	11.62[F]	9.5[G]	–
(2)	10.45 ± 0.05[C]	8.74 ± 0.02[C]	8.87 ± 0.11[C]
(3)	11.32 ± 0.02[C]	9.79 ± 0.02[C]	8.50 ± 0.03[C]
(4)	12.07[D]	10.59[H]	–

[A] The supporting electrolyte in this work was $NaNO_3$. In the literature studies other 1 : 1 electrolytes were used. [B] Ref. [2]. [C] This work. [D] Ref. [5]. [E] Ref. [16]. [F] Ref. [3]. [G] Ref. [1]. [H] Ref. [10].

(8).H_2^{2+} is much less. This is consistent with protonation of the primary amines ensuring less charge repulsion and a higher value for pK_{a2}. The decrease in (8).H_3^{3+} pK_{a3} is much larger because of increased charge proximity, but its magnitude is still much greater than those of (2).H_3^{3+}, (3).H_3^{3+}, and (4).H_3^{3+} (where in the latter case pK_{a3} was too small to be detected by our method) which have a closer charge proximity because of their macrocyclic structure.

Potentiometric Determinations of Zn^{2+} and Cd^{2+} Complexation by (2) and (3)

The titration curves for the formation of $[Cd.(2)]^{2+}$ and $[Cd.(3)]^{2+}$ are shifted to a lower pH by comparison with those for the deprotonation of (2).H_3^{3+} and (3).H_3^{3+}, respectively, consistent with Cd^{2+} competing strongly with H^+ for tetradentate (2) and pentadentate (3) (Fig. 1). The titration curves for the formation of $[Zn.(2)]^{2+}$ and $[Zn.(3)]^{2+}$ are further shifted to a lower pH consistent with these complexes being more stable than their Cd^{2+} analogues. In addition, there is a flattening of the $[Zn.(2)]^{2+}$ and $[Zn.(3)]^{2+}$ titration curves in the pH range 8–10 consistent with the occurrence of deprotonation of $[Zn.(2)]^{2+}$ and $[Zn.(3)]^{2+}$. The complexation of Zn^{2+} and Cd^{2+} by (2) and (3) are characterized by complexation constants, K_{Zn} and K_{Cd}, determined from the titration curves shown in Figure 1.These are shown in Table 1 together with those reported for (1) and (4)[1,3,5,10] and two pK_a values pertaining to deprotonations of $[Zn(2)]^{2+}$ and $[Zn(3)]^{2+}$. Several factors determine the magnitude of K_{Zn} and K_{Cd}, among which are the variations in basicity of the amine nitrogens as they are substituted with pendant hydroxyethyl arms and the consequent increase in the number of donor groups and the change from the borderline hard Lewis acid Zn^{2+} to the softer Cd^{2+}. This results in the magnitudes of K_{Zn} and K_{Cd} varying with the ligand in the sequence (1) > (2) < (3) < (4) such that the change of ligand is accompanied by more than an order of magnitude change in K_{Zn} and K_{Cd}. The competing effects of the decrease in the basicity of the nitrogens with pendant arm substitution are increasingly offset by the increase in ligand denticity. The smaller size and greater Lewis acidity of Zn^{2+} by comparison with Cd^{2+} results in $K_{Zn} \geq 500\, K_{Cd}$ for each ligand. The overall effect is that $[Zn.(4)]^{2+}$ is the most stable complex and $[Cd.(1)]^{2+}$ is the least stable. (For $[Zn.(8)]^{2+}$, $\log K_{Zn} = 8.8$ is significantly smaller because of the absence of a macrocyclic effect.[16])

The proton dissociations characterized by pK_a values of 8.87 and 8.50 for $[Zn.(2)]^{2+}$ and $[Zn.(3)]^{2+}$ could either arise from deprotonation of coordinated water or of the pendant arm hydroxy group. (The former is possible for $[Zn.(1)]^{2+}$ but not for $[Zn.(4)]^{2+}$ and vice versa.) Thus, either polarization of the hydroxyl O–H bond is decreased in $[Zn.(4)]^{2+}$ by comparison with those in $[Zn.(2)]^{2+}$ and $[Zn.(3)]^{2+}$, which is contrary to the trend predicted by the decrease in pK_a from $[Zn.(2)]^{2+}$ to $[Zn.(3)]^{2+}$, or the absence of coordinated water in $[Zn.(4)]^{2+}$ precludes its deprotonation and the observed pK_as are those of coordinated water in $[Zn.(2)]^{2+}$ and $[Zn.(3)]^{2+}$ with the inference that $[Zn.(2)]^{2+}$ is either five- or six-coordinate and $[Zn.(3)]^{2+}$ is six-coordinate. The latter interpretation raises the question as to why no deprotonation was observed for $[Zn.(1)]^{2+}$ which should have at least one water coordinated.[3] A comparison with the five-coordinate Zn^{2+} complexes of tripodal 2,2′,2″-triaminotetraethylamine and 2,2′,2″-tri(*N*,*N*-dimethylamine)triaminotetraethylamine, in which the pK_as of coordinated water are 10.26 and 9.00, respectively,[17] suggests that coordinated water becomes less acidic as its environment becomes less constrained and less hydrophobic. On this basis it is possible that the pK_a is $\geq$10 for coordinated water in $[Zn.(1)]^{2+}$. It is of interest that for the more hydrophobic 1,5,9-triazacyclododecane analogues of $[Zn.(1)]^{2+}$ and $[Zn.(2)]^{2+}$, their pK_a values of 7.3 and 7.4 are attributed to deprotonation of coordinated water and the pendant arm hydroxy group, respectively.[18,19]

Conclusion

This study of the protonation and metal ion complexation of the new ligands (2) and (3) provides a foundation for studies of ternary complex formation. The reliable syntheses of (2) and (3) provide an opportunity to substitute mixed pendant arms onto the 1,4,7-triazacyclononane platform which may act independently or cooperatively as receptors for metal ions and other guest species.

Experimental

Syntheses

1,4,7-Triazatricyclo[5.2.1.$0^{4,10}$]decane,[20] 1-formyl-1,4,7-triazacyclononane,[15] 1,4,7-triazacyclononane trihydrobromide, and 1,4,7-tris(2-hydroxyethyl)-1,4,7-triazacyclononane[5] were synthesized by methods similar to those reported in the literature. Solvents were purified by literature methods[21] and other reagents (Aldrich) were used without further purification.

1-Formyl-4,7-bis(2-hydroxyethyl)-1,4,7-trazacyclononane (7)

Ethylene oxide (0.40 cm^3, 8.01 mmol) in chilled ethanol (2.5 cm^3) was mixed with 1-formyl-1,4,7-triazacyclononane (0.21 g, 1.36 mmol) in ethanol at 0°C and stirred for 72 h in a stoppered flask at ambient temperature. Removal of ethanol under reduced pressure gave the title compound as a viscous oil which was dried under high vacuum at 80°C for 6 h (0.33 g, quantitative). ν_{max} (neat)/cm^{-1} 3396 (OH), 1655 (C=O); δ_H (600 MHz, $CDCl_3$) 2.59 (2 H, m, C(3)H_2), 2.64 (2 H, m, C(4)H_2), 2.74 (2 H, t, *J* 5.4, C(8)H_2), 2.78 (2 H, t, *J* 5.4, C(10)H_2), 2.92 (2 H, m, C(5)H_2), 2.94 (2 H, m, C(2)H_2), 3.40 (2 H, m, C(6)H_2), 3.47 (2 H, m, C(1)H_2), 3.56 (2 H, t, *J* 5.4, C(9)H_2), 3.63 (2 H, t, *J* 5.4, C(11)H_2), 4.49 (2 H, br s, 2 × OH), 8.15 (1 H, s, HC(17)O); δ_C (300 MHz) 47.94 (C1), 51.30 (C6), 52.96 (C2), 54.31 (C4), 54.90 (C3), 55.44 (C5), 59.01 (C10), 59.20 (C11), 59.47 (C9), 59.82 (C8), 163.88 (HC(7)O); *m*/*z* (LSI) 246.1808 $(M + H)^+$. $C_{11}H_{24}N_3O_3$ requires 246.1818.

1,4-Bis(hydroxyethyl)-1,4,7-triazacyclononane Dihydrobromide (3).2HBr

Method 1. 1-Formyl-4,7-bis(2-hydroxyethyl)-1,4,7-triazacyclononane, (7) (0.394 g, 161 mmol) was refluxed in 3 mol dm^{-3} hydrobromic acid (25 cm^3) at 110°C for 2.5 h. Removal of the solvent under reduced pressure gave a brittle pale yellow solid which was recrystallized from water/ethanol to give (3).2 HBr as white crystals (0.351 g, 58%), mp 155–157°C. δ_H(300 MHz, D_2O) 3.30 (4 H, t, *J* 5.3, 2 × NCH_2CH_2OH pendant arm), 3.42 (4 H, s, 2 × NCH_2CH_2NH ring), 3.54 (8 H, m, 2 × $HNCH_2CH_2NCH_2$ ring), 3.60 (2 H, br s, 2 × OH), 3.98 (4 H, t, *J* 5.3, 2 × NCH_2CH_2OH pendant arm); δ_C (50.32 MHz) 43.84 (2 × $NHCH_2$ ring), 50.60 (2 × $HNCH_2CH_2N$ ring),

51.26 ($(CH_2)_2NH$ ring), 58.28 ($2 \times NCH_2CH_2OH$ pendant arm),), 59.28 ($2 \times NCH_2CH_2OH$ pendant arm); m/z (LSI) 218.1897 $(M + H)^+$. $C_{10}H_{24}N_3O_2$ requires 218.1868. (Found: C, 31.6; H, 6.9; N, 11.1%. $C_{10}H_{25}Br_2N_3O_2$ requires C, 31.7; H, 6.7; N, 11.1%).

Method 2. 1,4,7-Triazacyclononane trihydrobromide, (1).3HBr (5.08 g, 13.7 mmol) was added to a solution of sodium metal (0.66 g, 28.7 mmol) in dry ethanol (80 cm^3) and was stirred for 16 h. Sodium bromide was removed by gravity filtration and the solution was cooled to 0°C. Ethylene oxide (1.43 cm^3, 28.6 mmol) in chilled ethanol (5 cm^3) was added and the reaction mixture was stirred at room temperature in a stoppered flask for 96 h. The solvent was removed under reduced pressure to give a viscous oil which was dissolved in water and acidified to pH 2 with 3 mol dm^3 hydrobromic acid. Removal of the solvent under reduced pressure gave a brittle white solid which was recrystallized from ethanol to give (3).2 HBr as white crystals (2.37 g, 37%). The physical and spectroscopic data of the product were identical to those of (3).2 HBr obtained in method 1. Unfortunately, method 2 sometimes gave a mixture of (2).2 HBr and (3).2 HBr, which were difficult to separate.

1,4-Bis(hydroxyethyl)-1,4,7-triazacyclononane, (3), may be obtained as the free triamine by passing an aqueous solution of (3).2HBr down a column of Amberlite IRA–400 in the Na^+ form. Removal of water from the collected effluent under reduced pressure and extraction of the resulting white solid with chloroform gave a solution of (3) which was isolated as a white amorphous solid after the chloroform was removed under reduced pressure. ν_{max} (neat)/cm^{-1} 3338 (OH); δ_H (200 MHz, $CDCl_3$) 2.67 (4 H, t, J 5.1, $2 \times NCH_2CH_2OH$ pendant arm) 2.68 (4 H, s, $2 \times NCH_2CH_2NH$ ring), 2.77 (8 H, m, $2 \times HNCH_2CH_2NCH_2$ ring), 3.48 (2 H, br s, 2 × OH), 3.61 (4 H, t, J 5.1, $2 \times NCH_2CH_2OH$ pendant arm); δ_C (50.32 MHz) 47.74 ($2 \times NHCH_2$ ring), 53.42 ($2 \times HNCH_2CH_2N$ ring), 53.99 ($(CH_2)_2NH$ ring), 59.54 ($2 \times NCH_2CH_2OH$ pendant arm), 59.75 ($2 \times NCH_2CH_2OH$ pendant arm); m/z (EI) 218 (M^+, 100%), 187 (16), 129 (77), 88 (71), 58 (37), 44(18).

Potentiometric Titrations

Titration solutions were prepared in deionised water that was further purified using a MilliQ-Reagent system to produce water with a resistance of >15 MΩ cm. Ionic strength was adjusted to 0.10 mol dm^{-3} with $NaNO_3$. The reagents $NaNO_3$, $ZnSO_4$, and $CdSO_4$ were recrystallized from water, and dried to constant weight and stored under vacuum over P_2O_5. (CAUTION: Anhydrous nitrates are potentially explosive and should be handled with care.) Nitric acid (70%, Ajax) and sodium hydroxide (Convol) were used as received.

Potentiometric titrations were carried out using a Metrohm E665 Dosimat autoburette interfaced to a Laser XT/3-8086 PC in conjunction with an Orion SA720 potentiometer and an Orion Ross Sureflow combination electrode. Values of E_0 and pK_w were determined by titration of a solution that was 3.00×10^{-3} mol dm^{-3} in HNO_3 and 0.05 mol dm^{-3} in $NaNO_3$ against 0.05 mol dm^{-3} NaOH. Titration solutions were thermostatted at 298.2 ± 0.05 K in a closed water jacketed vessel which had a small vent for the nitrogen stream which was passed through aqueous 0.10 mol dm^{-3} $NaNO_3$ prior to being bubbled through the magnetically stirred titration solutions to exclude atmospheric carbon dioxide. The instrumentation was calibrated by titration of 0.100 mol dm^{-3} NaOH (1.00 cm^3) from the autoburette against 0.004 mol dm^{-3} HNO_3 (10.00 cm^3). The pK_a values of (2).H_3^{3+} and (3).H_3^{3+} were determined by titration of 10.0 cm^3 solutions of 1.00×10^{-3} mol dm^{-3} in either (2) or (3) and 5.00×10^{-3} mol dm^{-3} in HNO_3 (such that the acid concentration was at least one mole in excess of that required to completely protonate the ligand) with 0.100 mol dm^{-3} NaOH. The stepwise complexation constants for the Zn^{2+} and Cd^{2+} complexes were determined at the same concentrations of (2) and (3) and HNO_3 in the presence of either 1.00×10^{-3} mol dm^{-3} $[Zn^{2+}]_{total}$ or $[Cd^{2+}]_{total}$. Generally the pH titration range was 2.00 to 10.5. The pK_as and stepwise Zn^{2+} complexation constants were derived using the program SUPERQUAD[22] and appear in Table 1.

Acknowledgments

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References

[1] T. Arishima, K. Hamada, S. Takamoto, *Bull. Chem. Soc. Jpn.* **1973**, 1119.
[2] R. L. Yang, L. J. Zompa, *Inorg. Chem.* **1976**, *15*, 1499.
[3] L. J. Zompa, *Inorg. Chem.* **1978**, *17*, 2531.
[4] P. Chaudhuri, K. Wieghart, Y.-H. Tsai, C. Kruger, *Inorg. Chem.* **1982**, *21*, 3086.
[5] B. A. Sayer, J. P. Michael, R. D. Hancock, *Inorg. Chim. Acta* **1983**, *77*, L63.
[6] A. A. Belal, L. J. Farrugia, R. D. Peacock, J. Robb, *J. Chem. Soc., Dalton Trans.* **1989**, 931.
[7] I. Fallis, J. Farrugia, N. M. McDonald, R. D. Peacock, *Inorg. Chem.* **1993**, *32*, 779.
[8] E. Cole, R. C. B. Copley, J. A. K. Howard, D. Parker, G. Ferguson, J. F. Gallagher, B. Kaitner, A. Harrison, L. Royale, *J. Chem. Soc., Dalton Trans.* **1994**, 1619.
[9] J. Huskens, A. D. Sherry, *J. Am. Chem. Soc.* **1996**, *118*, 4396.
[10] R. Luckay, R. D. Hancock, I. Cukrowski, J. H. Riebenspies, *Inorg. Chim. Acta*, **1996**, *246*, 159.
[11] A. A. Watson, A. C. Wills, D. P. Fairlie, *Inorg. Chem.* **1997**, *36*, 752.
[12] J. M. Weeks, M. A. Buntine, S. F. Lincoln, E. R. T. Tiekink, K. P. Wainwright, *J. Chem. Soc., Dalton Trans.* **2001**, 2157.
[13] J. M. Weeks, M. A. Buntine, S. F. Lincoln, K. P. Wainwright, *Inorg. Chim. Acta* **2002**, *331*, 340.
[14] S. P. Creaser, S. F. Lincoln, S. M. Pyke, *J. Chem. Soc., Perkin Trans. 1* **1999**, 1211.
[15] A. J. Blake, I. A. Fallis, R. O. Gould, S. Parsons, S. A. Ross, M. Schröder, *J. Chem. Soc., Chem. Commun.* **1994**, 2467.
[16] R. M. Smith, A. E. Martell, *Critical Stability Constants*, **1975**, Vol. 2, p101, (Plenum Press: New York, NY).
[17] J. H. Coates, G. J. Gentle, S. F. Lincoln, *Nature* **1974**, *249*, 773.
[18] E. Kimura, T. Shiota, T. Koike, M. Shiro, M. Kodama, *J. Am. Chem. Soc.* **1990**, *112*, 5805.
[19] E. Kimura, I, Nakamura, T. Koike, M. Shionoya, M. Kodama, *J. Am. Chem. Soc.* **1994**, *116*, 4764.
[20] (*a*) J. E. Richman, T. J. Atkins, *J. Am. Chem. Soc.* **1974**, *96*, 2268; (*b*) T. J. Atkins, J. E. Richman, W. F. Oettie, *Org. Synth.* **1978**, *58*, 86.
[21] D. D. Perrin, W. L. Armarego, *Purification of Laboratory Chemicals*, 3rd Edn, **1998** (Permagon Press: Oxford).
[22] P. Gans, A. Sabatini, A. Vacca, *J. Chem. Soc., Dalton Trans.* **1985**, 1195.