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Stability and Structure for Monomeric Cadmium(II) and Zinc(II) Complexes of the 5′-Triphosphates of Adenosine and Cytidine in Aqueous Solution: Isomeric Equilibria in Binary and Ternary Complexes

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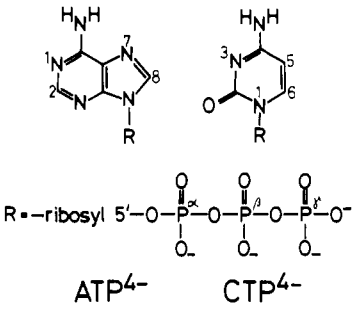
The experimental conditions were such that the concentration of the monomeric species of ATP or CTP (=NTP), as well as of their complexes, was strongly dominating. The acidity constants of $H_2(ATP)^{2-}$ in D_2O were determined by ^1H NMR shift measurements and potentiometric pH titrations and compared with the corresponding constants for H_2O as solvent. The reflection of the γ-phosphate deprotonation of $H(ATP)^{3-}$ in the chemical shift of H-8 is possibly an indication for a weak hydrogen bond involving the phosphate chain and N-7. The stability constants of $Cd(H{\cdot}NTP)^-$, $Cd(NTP)^{2-}$, $Cd(bpy)(H{\cdot}NTP)^-$, and $Cd(bpy)(NTP)^{2-}$ (where bpy = 2,2′-bipyridyl) were determined for aqueous solution and compared with the corresponding values of the Zn^{2+} complexes; to a first approximation the stabilities of the Cd^{2+} and Zn^{2+} complexes are comparable. The binary Cd^{2+} and Zn^{2+} complexes, $M(CTP)^{2-}$, are somewhat less stable than $M(ATP)^{2-}$; this is due to an intramolecular equilibrium between a phosphate-coordinated $M(ATP)^{2-}$ isomer and an isomer in which M^{2+} interacts in addition with the base residue to form a macrochelate (about 50% for the Cd^{2+} system). In the ternary $M(bpy)(NTP)^{2-}$ complexes the metal ion/base interaction is inhibited; all these ternary complexes (M^{2+} = Cd^{2+} or Zn^{2+}; NTP^{4-} = CTP^{4-} or ATP^{4-}) undergo to a significant extent (about 60%) an intramolecular stacking interaction; i.e., the aromatic base residue stacks with 2,2′-bipyridyl. ^1H NMR shift experiments in D_2O also show that formation of the simple ternary hydroxo complexes $Cd(ATP)(OH)^{3-}$ and $Zn(ATP)(OH)^{3-}$ is connected with a release of N-7 from the coordination sphere of the metal ion. All these results are further indications for the high versatility of ATP as a ligand.

It appears that all enzymic reactions involving nucleotides, in particular ATP,[2] are metal ion dependent.[3-6] Indeed, in the case of ATP, its complexes are usually the substrates. Hence, the wide interest that ATP and other nucleotide complexes are receiving[7-10] is certainly justified.

Our studies on the metal ion promoted dephosphorylation of nucleoside 5′-triphosphates (NTP),[11,12] which includes also Cd^{2+},[13] are one reason for our interest in the properties of Cd^{2+}/ATP complexes. The other reason is that Cd^{2+}, although chemically related to the biologically important Zn^{2+}, is a highly toxic metal ion,[14,15] with some indications of being also one of the ultratrace elements.[16-18] Hence, it seems desirable to accumulate more comparable knowledge on the interaction between Cd^{2+} and biomolecules.

It is now well-known[19] that metal ions, including Cd^{2+}, promote the self-association of ATP, which occurs via stacking of the purine residues. Hence, studies on the properties of monomeric $Cd(ATP)^{2-}$ and related complexes require concentrations smaller than 10^{-3} M. Under these conditions about 96% or more of the complexes are present in their monomeric form.[19] An evaluation of the literature, taking into account only those studies[20-23] in which the monomeric forms strongly dominated, revealed[19] that the divalent metal ions of the second half of the first transition series, including Zn^{2+}, form macrochelated complexes. This means the metal ions are coordinated to the triphosphate chain and partly also to N-7 of the adenine residue.

Chart I



This metal ion/base interaction gives rise to intramolecular equilibria that also occur with $Cd(ATP)^{2-}$ and $Zn(ATP)^{2-}$. The positions of these equilibria are estimated in the present study by including the M^{2+}/CTP systems (Chart I). It is also shown that formation of the ternary Cd^{2+} and Zn^{2+} complexes with 2,2′-bipyridyl or OH^- prevents any metal ion/base interaction. The stabilities and structures for the binary and ternary complexes of the two Cd^{2+}/NTP systems are compared with the corresponding complexes containing Zn^{2+}.

Experimental Section

Materials. The disodium salt of adenosine 5′-triphosphate (>98%; p.A.) and cytidine 5′-triphosphate (for biochemistry) were purchased from Serva Feinbiochemica GmbH, Heidelberg. The nitrate salts of Na^+, Cd^{2+}, and Zn^{2+}, the disodium salt of EDTA, 2,2′-bipyridyl, HNO_3, NaOH (Titrisol) (all p.A.), DNO_3 and NaOD (both with >99% D), and a 10% tetramethylammonium hydroxide solution (p.A.)

(1) (a) University of Basel. (b) Boston University.
(2) Abbreviations: ATP, adenosine 5′-triphosphate; bpy, 2,2′-bipyridyl; CTP, cytidine 5′-triphosphate; M^{2+}, general divalent metal ion; NTP = ATP, CTP, and/or UTP; UTP, uridine 5′-triphosphate. The phosphate groups in NTP are labeled as α, β, and γ, where the latter refers to the terminal phosphate group.
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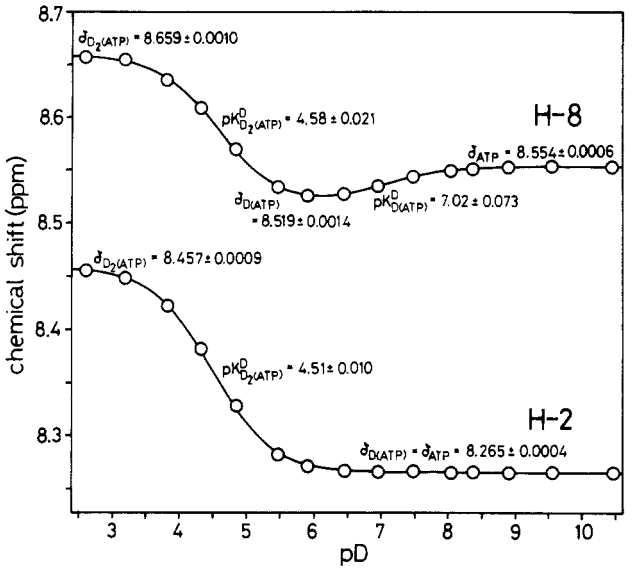

Figure 1. Dependence of the chemical shifts of H-2 and H-8 for ATP on pD. The ^1H NMR spectra were measured in D_2O at $[ATP]_{tot} = 5 \times 10^{-3}$ M[29] ($I = 0.1$ ($NaNO_3$); 25 °C). The curves shown are the computer-calculated best fits through the experimental data (○), which have led to the inserted chemical shifts, δ, and the values for pK_A; all errors given correspond to a single standard deviation. The weighted mean of the acidity constants is listed in Table I.

(which was converted into the nitrate) were obtained from Merck AG, Darmstadt, FRG. D_2O (≥99.8%) was from CIBA-Geigy AG, Basel, Switzerland.

The titer of NaOH used for the titrations was determined with potassium hydrogen phthalate (Merck AG); the exact concentrations of the NTP solutions used in the titrations with metal ions (titrated in the presence of an excess of HNO_3; see below) were measured by titrations with NaOH. The concentrations of the stock solutions of the divalent metal ions were determined with EDTA.

All experiments with ATP or CTP were done in such a way that dephosphorylation of these 5′-triphosphates, which is metal ion promoted,[13] was kept to a minimum.

Potentiometric pH Titrations. The pH titrations were carried out with a Metrohm potentiograph E536 and a Metrohm macro EA 121 glass electrode. The buffers (pH 4.64, 7.00, and 9.00) used for calibration were also from Metrohm AG. The direct pH meter readings were used in the calculations for the acidity constants.

The acidity constants $K^H_{H_2(NTP)}$ and $K^H_{H(NTP)}$ for $H_2(NTP)^{2-}$ were determined by titrating 50 mL of aqueous 0.9 mM HNO_3 and $NaNO_3$ ($I = 0.1$; 25 °C) in the presence and absence of 0.4 or 0.6 mM NTP^{4-} under N_2 with 1 mL of 0.05 M NaOH. The acidity constants were calculated from seven independent titrations within the range of about 25% neutralization for the equilibrium $H_2(NTP)^{2-}/H(NTP)^{3-}$ (lower values are not reached under the given conditions) to 98% for the equilibrium $H(NTP)^{3-}/NTP^{4-}$. (For the measurements in D_2O see section 1.)

The conditions for the determination of the stability constants $K^{Cd}_{Cd(H\cdot NTP)}$ and $K^{Cd}_{Cd(NTP)}$ in the binary Cd^{2+}/NTP systems were the same as for the acidity constants, the $[Cd^{2+}]$:[NTP] ratios being always 1:1. The stability constants were computed from four independent titrations for each system with a curve-fitting procedure[24] that became satisfactory by taking into account the species H^+, $H_2(NTP)^{2-}$, $H(NTP)^{3-}$, NTP^{4-}, Cd^{2+}, $Cd(H\cdot NTP)^-$, and $Cd(NTP)^{2-}$. From the upper pH range a value for $Cd(NTP)(OH)^{3-}$ was also estimated.

The ternary Cd^{2+}/2,2′-bipyridyl/NTP systems were titrated four times in the ratio 1:1:1 ([reactant] = 0.4 mM). In the curve-fitting procedure[24] the following species were taken into account: H^+, $H_2(NTP)^{2-}$, $H(NTP)^{3-}$, NTP^{4-}, $H_2(bpy)^{2+}$, $H(bpy)^+$, bpy, Cd^{2+}, $Cd(H\cdot NTP)^-$, $Cd(NTP)^{2-}$, $Cd(bpy)^{2+}$, $Cd(bpy)_2^{2+}$, $Cd(bpy)(H\cdot NTP)^-$, and $Cd(bpy)(NTP)^{2-}$. The constants for the binary Cd^{2+}/bpy system were taken from the work of Anderegg.[25-27]

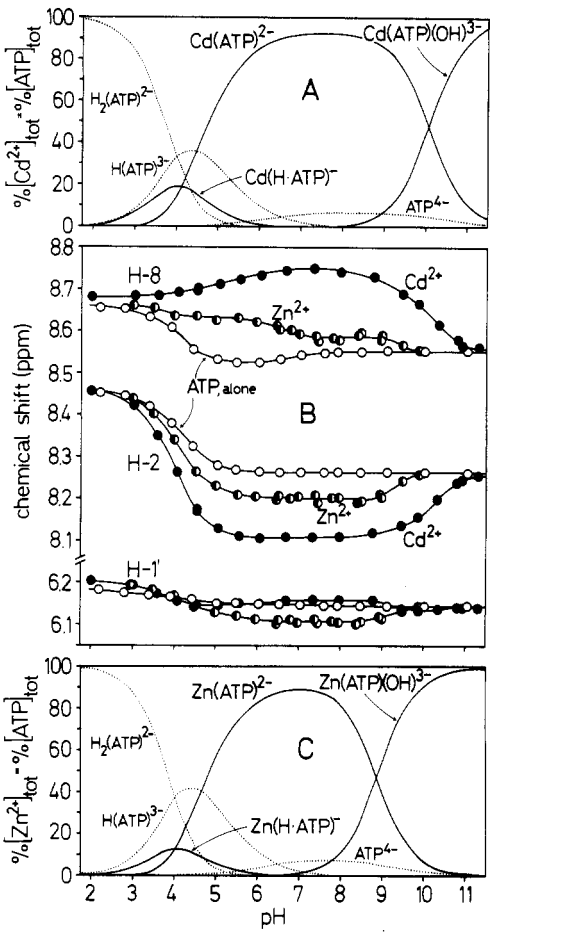

Figure 2. Comparison of the variation (B) of the chemical shift of H-2, H-8, and H-1′ in the ^1H NMR spectra of ATP (○/5×10^{-3} M) and of ATP in the presence of Cd^{2+} (●/$1{:}1/5 \times 10^{-3}$ M) or Zn^{2+} (◐/$1{:}1/5 \times 10^{-3}$ M) in D_2O at 27 °C ($I = 0.1$ ($NaNO_3$)) as a function of "pH" (i.e., no correction was applied to the pH meter reading)[58] with the effect of pH at 25 °C ($I = 0.1$) on the concentration of the species present in an aqueous solution of Cd^{2+} and ATP (each 10^{-3} M) (A) and Zn^{2+} and ATP (each 10^{-3} M) (C). The results are given as the percentage of the total M^{2+} present (=total ATP). The broken lines indicate the free ATP species and the solid lines the ATP complexes. The species distribution for both M^{2+}/ATP systems was calculated with the constants listed in Tables I and II. Diprotonated complexes of the type $M(H_2ATP)$ were ignored in these calculations as the appropriate constants are unknown; however, such species would probably exist only below pH 3.

^1H NMR Shift Measurements. The ^1H NMR spectra were recorded with a Bruker WH-90 FT spectrometer (90.025 MHz) at 27 °C, using the center peak of the tetramethylammonium ion triplet as internal reference. All chemical shifts were converted to a (trimethylsilyl)-propanesulfonate reference by adding 3.188 ppm. The reliability of tetramethylammonium ion as an internal ^1H NMR reference in such studies has been discussed previously in detail.[19]

The pD of the solutions was obtained by adding 0.40 to the pH meter reading.[28] The pH was measured with a Metrohm glass electrode EA 125. The experiments were carried out as described;[19] additional details are given in the legends for Figures 1 and 2.

Results and Discussion

A precondition for any study of a metal ion/ligand interaction is the detailed knowledge of the basicity properties of the ligand. Therefore, we have first determined the pK_A values of $H_2(ATP)^{2-}$ in D_2O and water (section 1) before progressing

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(26) Stability constants: $\log K^{Cd}_{Cd(bpy)} = 4.25$, $\log K^{Cd(bpy)}_{Cd(bpy)_2} = 3.6$. Acidity constant: $pK^H_{H(bpy)} = 4.49$ ($I = 0.1$ ($NaNO_3$); 20 °C);[25] $pK^H_{H_2(bpy)} = -0.2$ (from ref 27) does not play a role in the calculations.

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Table I. Negative Logarithms of the Acidity Constants of $H_2(ATP)^{2-}$ As Determined by Potentiometric pH Titrations in Water (I = 0.1 ($NaNO_3$ or $NaClO_4$); 25 °C) and D_2O (I = 0.1 ($NaClO_4$); 25 °C) and by ^1H NMR Shift Measurements in D_2O (I = 0.1 ($NaNO_3$); 27 °C)[a]

		pH titration		
pK_A	eq	H_2O	D_2O	^1H NMR
$pK^H_{H_2(ATP)}$	1	4.03 ± 0.02	4.54 ± 0.02	4.53 ± 0.03
$pK^H_{H(ATP)}$	2	6.51 ± 0.01	7.04 ± 0.01	7.02 ± 0.22

[a] The errors given are 3 times the standard error of the mean value or the sum of the probable systematic errors, whichever is larger. The results given for the ^1H NMR measurements are the weighted means of the data shown in Figure 1.

to the stability of binary and ternary M^{2+}/NTP complexes (section 2) and to the evaluation of their structures (sections 3–5).

1. Acidity Constants of $H_2(ATP)^{2-}$ in D_2O and Water. As the ^1H NMR shift experiments for the Cd^{2+} and Zn^{2+}/ATP systems (section 5) had to be carried out in D_2O, we determined the acidity constants of $H_2(ATP)^{2-}$ by ^1H NMR in the same solvent and also independently by potentiometric pH titrations in D_2O and in H_2O.

The potentiometric titrations were carried out with 2.4 × 10^{-3} M solutions of ATP. Under these conditions no notable self-association occurs.[19,29] The titrations (I = 0.1; 25 °C) reveal in accordance with earlier studies[10] that for ATP in the range pH 3.5–8 the following two protonation equilibria occur:

$$H_2(NTP)^{2-} \rightleftharpoons H(NTP)^{3-} + H^+$$
$$K^H_{H_2(NTP)} = [H(NTP)^{3-}][H^+]/[H_2(NTP)^{2-}] \quad (1)$$

$$H(NTP)^{3-} \rightleftharpoons NTP^{4-} + H^+$$
$$K^H_{H(NTP)} = [NTP^{4-}][H^+]/[H(NTP)^{3-}] \quad (2)$$

The corresponding acidity constants are listed in Table I. The acidity constants, $K^H_{H_2(NTP)}$, determined for the first buffer region are due to the release of a proton from the protonated base moiety, i.e. from N-1 in $H_2(ATP)^{2-}$, while $K^H_{H(NTP)}$ reflects the removal of a proton from the terminal γ-phosphate group of the $H(ATP)^{3-}$ species;[10] this attribution agrees with the ^1H NMR shift experiments.

The pH dependency of the chemical shifts of H-2 and H-8 of ATP (5 × 10^{-3} M)[29] as shown in Figure 1 allows one to determine, by a curve-fitting procedure, the first acidity constant of $D_2(ATP)^{2-}$ from both H-2 and H-8. The weighted mean gives $pK^D_{D_2(ATP)}$ = 4.53 ± 0.03, which is an excellent agreement with the value obtained from the potentiometric pH titrations (Table I). Evaluation of the chemical shift of H-8 upon the triphosphate deprotonation gives $pK^D_{D(ATP)}$ = 7.02 ± 0.22 (eq 2), also in perfect agreement with the result of the potentiometric titrations (Table I). The relatively large error is due to the small shift differences of H-8 between $D(ATP)^{3-}$ (δ 8.519 ± 0.004) and ATP^{4-} (δ 8.554 ± 0.002) (Figure 1).

The difference $\Delta pK_A = pK^D_A - pK^H_A$ from Table I, which characterizes the isotope effect, becomes 0.51 and 0.53 for the N-1 and γ-phosphate deprotonations, respectively. The latter difference is in excellent agreement with an earlier determination[31] of 0.54 log unit. The differences for the two very different kinds of acidic groups both agree closely with a suggested correlation[32] of $\Delta pK_A = 0.45 + 0.015 pK^H_A$.

The sensitivity of the chemical shift of H-8 toward deprotonation of the γ-phosphate group in $D(ATP)^{3-}$ and especially the fact that upon deprotonation a *down*field shift occurs are somewhat surprising,[33] although this effect has been observed before for $H(ATP)^{3-}$ (ref 36) and $H(AMP)^-$ (see Figure 5 in ref 37). A possible explanation for this unexpected downfield shift would be the formation of a weak *intra*molecular hydrogen bond in $H(ATP)^{3-}$ between the proton at the γ-phosphate group and N-7 of the adenine moiety, possibly with a water molecule in between. With such a weak interaction H-8 would be shielded under the influence of the negative charge(s) of the phosphate residue, while upon deprotonation of the γ group the hydrogen bond would be lost and the negative charge(s) of the phosphate residue removed, initiating in this way a downfield shift. Indications for an intramolecular hydrogen bond to N-7 have also been given[38] for $H(1,N^6$-etheno-$ATP)^{3-}$. Another and maybe more satisfactory explanation would be that upon deprotonation of the γ-phosphate group a conformational change occurs and that a weak hydrogen bond involving a water molecule between N-7 and the ionized phosphate moiety is formed. This interpretation could also account for the observed downfield shift, because the reaction $H(ATP)^{3-} \rightarrow ATP^{4-}$ would become connected with hydrogen-bond formation at N-7.

2. Stability of the Cd^{2+} Complexes of ATP and CTP together with the Stability of the Corresponding Ternary Complexes Containing 2,2′-Bipyridyl. For reasons of comparison (see section 3) the Cd^{2+}/CTP system was included in these measurements. The experimental data of the potentiometric pH titrations for both Cd^{2+}/NTP 1:1 systems are completely described by the equilibria (3)–(5). The acidity constant of

$$M^{2+} + H(NTP)^{3-} \rightleftharpoons M(H{\cdot}NTP)^-$$
$$K^M_{M(H{\cdot}NTP)} = [M(H{\cdot}NTP)^-]/[M^{2+}][M(NTP)^{3-}] \quad (3)$$

$$M^{2+} + NTP^{4-} \rightleftharpoons M(NTP)^{2-}$$
$$K^M_{M(NTP)} = [M(NTP)^{2-}]/[M^{2+}][NTP^{4-}] \quad (4)$$

$$M(NTP)_{aq}^{2-} \rightleftharpoons M(NTP)(OH)^{3-} + H^+$$
$$K^H_{M(NTP)(H_2O)} = [H^+][M(NTP)(OH)^{3-}]/[M(NTP)^{2-}] \quad (5)$$

the connected equilibrium 6 may be calculated with eq 7. For

$$M(H{\cdot}NTP)^- \rightleftharpoons M(NTP)^{2-} + H^+$$
$$K^H_{M(H{\cdot}NTP)} = [H^+][M(NTP)^{2-}]/[M(H{\cdot}NTP)^-] \quad (6)$$

$$pK^H_{M(H{\cdot}NTP)} = pK^H_{H(NTP)} + \log K^M_{M(H{\cdot}NTP)} - \log K^M_{M(NTP)} \quad (7)$$

the equilibrium constants of the ternary Cd(bpy)$(H{\cdot}NTP)^-$ and Cd(bpy)$(NTP)^{2-}$ complexes, the definitions given for the

(29) In a 5 × 10^{-3} M solution of ATP at pD 8.4, about 99% of the ATP occurs in the monomeric form (calculated with K = 1.3 M^{-1}).[19] As this result applies to $Na(ATP)^{3-}$ rather than to ATP^{4-} (see footnote 51 in ref 19), one may in addition conclude that the given value will also hold approximately for $H(ATP)^{3-}$ (as the charge neutralization, which plays a significant role in the self-association, is the same) while the self-association of ATP^{4-} will even be smaller. However, one should also mention in this connection that preliminary experiments on a Varian Anaspect EM-360 spectrometer (60 MHz) at 34 °C in D_2O at pD 3.0 with ATP in the concentration range of 0.019–0.2 M (natural ionic strength) show that the self-association tendency of $H_2(ATP)^{2-}$ is larger: $K \geq 20$ M^{-1} (as defined by the isodesmic model for an indefinite noncooperative association; see ref 19). This latter value is also larger than the one of AMP^{2-} (K = 2.1 M^{-1}). This observation agrees with a CD study[30] at pH 2.8 and 20 °C.

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Table II. Logarithms of the Stability Constants of the Binary Cd^{2+} Complexes with ATP and CTP, As Well As of the Corresponding Ternary Complexes Containing also 2,2'-Bipyridyl ($I = 0.1$ ($NaNO_3$); 25 °C)[a,b] (Values in Parentheses for the Corresponding Zn^{2+} Complexes)

	eq	ATP	CTP[b]
$\log K^{Cd}_{Cd(H\cdot NTP)}$	3	2.95 ± 0.09 (2.67)[c]	3.16 ± 0.04 (2.98)[d]
$\log K^{Cd}_{Cd(NTP)}$	4	5.31 ± 0.02 (5.16)[d]	4.99 ± 0.01 (4.79)[d]
$pK^{H}_{Cd(H\cdot NTP)}$	6, 7	4.15 (4.02)	4.71 (4.73)
$pK^{H}_{Cd(NTP)(H_2O)}$	5	10.1 (8.87)[e]	10.0 (8.79)[e]
$\log K^{Cd(bpy)}_{Cd(bpy)(H\cdot NTP)}$		2.61 ± 0.04	2.75 ± 0.11 (3.02)[d]
$\log K^{Cd(bpy)}_{Cd(bpy)(NTP)}$		4.98 ± 0.01 (5.26)[d]	4.95 ± 0.02 (5.14)[d]
$pK^{H}_{Cd(bpy)(H\cdot NTP)}$		4.14	4.34 (4.42)

[a] The errors given are 3 times the standard error of the mean value. If no error limit is given, the constant has been calculated from values listed above or in Table I. [b] The acidity constants of $H_2(CTP)^{2-}$ (eq 1 and 2) are $pK^{H}_{H_2(CTP)} = 4.53 \pm 0.02$ (due to the release of the proton located at N-3) and $pK^{H}_{H(CTP)} = 6.54 \pm 0.01$ (corresponding to the removal of the proton from the γ-phosphate group). The acidity constants of $H_2(ATP)^{2-}$ are listed in Table I. For the constants of the binary Cd^{2+}/bpy system, see ref 26. [c] Reference 39. [d] Reference 40. [e] Reference 41.

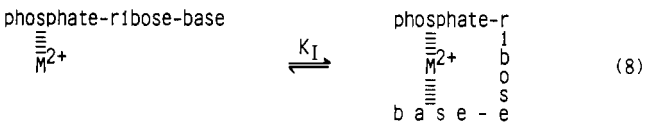
binary systems in eq 3, 4, 6, and 7 also apply, but M^{2+} has to be replaced by $Cd(bpy)^{2+}$. The constants for the ternary complexes were calculated by taking into account the known[26] constants of the Cd^{2+}/bpy system. All the results are listed in Table II.

A comparison of the acidity constants for eq 6 with those of eq 1 shows that $Cd(H\cdot ATP)^-$ is 0.12 log unit less acidic than $H_2(ATP)^{2-}$ (Table I and II); the corresponding difference for the CTP systems is 0.18 log unit (Table II). This observation suggests that in $Cd(H\cdot ATP)^-$ and $Cd(H\cdot CTP)^-$ the proton is mainly located at the γ-phosphate group, though a smaller amount of the isomeric species with the proton at the base moiety may still occur; this interpretation is in line with the ^1H NMR shift data discussed in section 5. The slightly greater stability of $Cd(H\cdot CTP)^-$ compared with $Cd(H\cdot ATP)^-$ reflects the small difference in the values of $pK^{H}_{H_2(NTP)}$ (Tables I and II).

A comparison of the corresponding constants in Table II for the Cd^{2+} and Zn^{2+} complexes[39-41] reveals that to a first approximation complex stability is very similar for both metal ions. However, it appears that the binary Zn^{2+}/NTP complexes are somewhat less stable than the corresponding Cd^{2+} complexes, while for the ternary complexes with 2,2'-bipyridyl the Cd^{2+} complexes appear as slightly more stable.

3. Extent of Intramolecular Macrochelate Formation in $Cd(ATP)^{2-}$. The acidity constants of $H(ATP)^{3-}$ and $H(CTP)^{3-}$ are nearly identical, while the stability of $Cd(ATP)^{2-}$ is by about 0.3 log unit larger than that of $Cd(CTP)^{2-}$. The increased stability of the ATP complex corresponds to the general experience[19,23] with divalent transition-metal ions and is attributed to the participation of N-7 of the adenine moiety in complex formation; no metal ion/base interaction has so far been observed in any of the $M(CTP)^{2-}$ complexes studied,[19,23,42,43] including an ^1H NMR shift study[19] of $Cd(CTP)^{2-}$.[44,46]

To quantify the extent of the metal ion/base interaction in $Cd(ATP)^{2-}$ we consider the intramolecular equilibrium (8) between an "open" isomer, $M(ATP)^{2-}_{op}$, and a "closed" species, $M(ATP)^{2-}_{cl}$. It was recently shown[23] that the dimensionless



(8)

intramolecular equilibrium constant K_I can be deduced[43,47-50] from the experimentally accessible overall stability constant, $K^{M}_{M(ATP)}$ (eq 4), by using eq 9, provided the stability constant,

$$K_I = \frac{[M(ATP)^{2-}_{cl}]}{[M(ATP)^{2-}_{op}]} = \frac{K^{M}_{M(ATP)}}{K^{M}_{M(ATP)_{op}}} - 1 \qquad (9)$$

$K^{M}_{M(ATP)_{op}}$, of the "open" isomer $M(ATP)^{2-}_{op}$ is also known. As the acidity constants for $H(ATP)^{3-}$ and $H(CTP)^{3-}$ are practically identical (Tables I and II), $K^{Cd}_{Cd(ATP)_{op}}$ will be well described by the value of $K^{Cd}_{Cd(CTP)_{op}}$, and one obtains then $K_I = 1.09$ for the isomeric $Cd(ATP)^{2-}_{cl}/Cd(ATP)^{2-}_{op}$ system.

From the given K_I value one calculates that 52% of $Cd(ATP)^{2-}$ exists in the macrochelated form (eq 8), a result in excellent agreement with the 54% estimated from ^1H NMR shift data.[19] In addition, this value is of the same order as the 62% estimated[19] (also with eq 9) for the closed isomer of $Zn(ATP)^{2-}$.

4. Stability and Structure of Ternary $M(bpy)(NTP)^{2-}$ Complexes. The stability of such ternary complexes (Table II) is best quantified by determining the position of equilibrium 10. The corresponding equilibrium constant $10^{\Delta \log K}$ is cal-

$$M(bpy)^{2+} + M(NTP)^{2-} \rightleftharpoons M(bpy)(NTP)^{2-} + M^{2+} \qquad (10)$$

culated[50-52] with eq 11. The value expected for $\Delta \log K$ on

$$\Delta \log K = \log K^{M(bpy)}_{M(bpy)(NTP)} - \log K^{M}_{M(NTP)} = \log K^{M(NTP)}_{M(NTP)(bpy)} - \log K^{M}_{M(bpy)} \qquad (11)$$

a statistical basis[52] may be obtained by assuming an octahedral coordination sphere for the metal ion, a bidentate coordination of bpy, and a tridentate coordination of NTP^{4-}: $\Delta \log K_{statist} = -0.78$.

From the stability constants listed in Table II one may calculate with eq 11 $\Delta \log K$ for the ternary systems of Cd^{2+}/bpy/ATP^{4-} and Cd^{2+}/bpy/CTP^{4-}. The corresponding

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(46) This experience regarding the $M(CTP)^{2-}$ and $M(ATP)^{2-}$ complexes may be rationalized by the conformation that nucleotides adopt in aqueous solution, i.e., by the relative orientation of the base and sugar rings about the N-1/C-1' bond in pyrimidines and about the N-9/C-1' bond in purines.[10] From the two main conformations, syn and anti, the latter is favored in aqueous solution. In this anti conformation the N-1/C-6 bond of pyrimidines and the N-9/C-8 bond of purines project onto or near the sugar ring;[10] consequently, the N-3 of pyrimidine nucleotides is directed away from the phosphate moiety while in purine nucleotides N-7 is orientated toward the phosphate residue.
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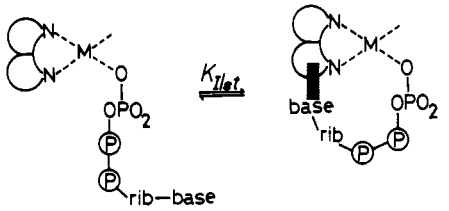
Table III. Quantification of the Stability of Some Mixed-Ligand M(bpy)(NTP)$^{2-}$ Complexes Containing Zn^{2+} or Cd^{2+} by the Values of $\Delta \log K$ (Eq 11), together with the Estimated Percentage of the Isomer with an Intramolecular Stack (Eq 12) for the Corresponding Systems (I = 0.1; 25 °C)

M(bpy)(NTP)$^{2-}$	$\Delta \log K$	M(bpy)-(NTP)$_{stack}^{2-}$,[c] %
Cd(bpy)(CTP)$^{2-}$	−0.04[a]	55
Cd(bpy)(ATP)$^{2-}$	−0.33[a]	60
Zn(bpy)(CTP)$^{2-}$	0.35[b]	75
Zn(bpy)(UTP)$^{2-}$	0.15[b]	65
Zn(bpy)(ATP)$^{2-}$	0.10[b]	70

[a] Calculated with eq 11 from the data listed in Table II. [b] From ref 40. [c] These estimated percentages are based on the equation $K_{I/st} = 10^{\Delta\Delta \log K} - 1$.[34,35,50] The calculation procedure is indicated for two examples: (i) Assuming that to the total stability increase of 0.74 log unit [$=\Delta \log K - \Delta \log K_{statist} = -0.04 - (-0.78)$] observed for Cd(bpy)(CTP)$^{2-}$ the two effects mentioned in the text each contribute to about 50%, one obtains $\Delta\Delta \log K = 0.37$ log unit, i.e. $K_{I/st} \simeq 1.3$ corresponding to about 55% for the stacked isomer. (ii) For the Cd(bpy)(ATP)$^{2-}$ complex: stacking part = $\Delta\Delta \log K = \Delta \log K - \Delta \log K_{statist} + \log \Delta$ (due to the release of Cd^{2+} from N-7; see ref 53) − π stabilization (point i of the text; it is taken as 0.37 log unit as in the preceding estimation) = −0.33 − (−0.78) + 0.30 − 0.37 = 0.38. Hence, $K_{I/st} \simeq 1.4$ corresponding to about 60% for the stacked isomer of Cd(bpy)(ATP)$^{2-}$.

results are listed in Table III together with some related data. From $\Delta \log K_{Cd/bpy/ATP} = -0.33$ and $\Delta \log K_{Cd/bpy/CTP} = -0.04$ follows that in equilibrium 10 all four species occur simultaneously in appreciable amounts; furthermore, these values are larger than the value obtained from statistical considerations. This is even more evident for the Zn(bpy)(NTP)$^{2-}$ complexes, which give *positive* values for $\Delta \log K$. The higher stability of ternary Zn^{2+} complexes, compared with the Cd^{2+} complexes, if a heteroaromatic N ligand and an O ligand are involved in complex formation, is in agreement with earlier experience.[53]

The increased stability of all these ternary complexes may be attributed, due to previous experience,[51,52] to two different cooperative effects: (i) π-accepting heteroaromatic N bases (like 2,2′-bipyridyl) coordinated to a transition-metal ion favor the coordination of O donors (like phosphates);[53,54] (ii) intramolecular aromatic-ring stacking enhances the stability of ternary complexes.[34,35] Such intramolecular stacks have already been observed in solution[31,55,56] and in the solid state[57] for M/bpy/NTP^{2-} systems. Hence, in aqueous solution one has to consider the intramolecular equilibrium (12) for these



(12)

ternary complexes. By using the equations published earlier[34,50] one obtains the estimates given in the column at the right in Table III: for the ternary Zn^{2+} and Cd^{2+} complexes considered, between about 55 and 75% exist in the stacked isomeric form. These estimates are in fair agreement with the 40 and 55% estimated by ^{1}H NMR shift measurements[56] for the stacked isomer of Zn(bpy)(UTP)$^{2-}$ and Zn(bpy)(ATP)$^{2-}$, respectively. It may be added that some stacking is also expected in the protonated M(bpy)(H·NTP)$^-$ complexes; for Zn(bpy)(H·UTP)$^-$ this has already been proven by ^{1}H NMR.[56]

The points to be emphasized are that (i) all methods of estimation indicate a rather large amount for the stacked isomeric form of M(bpy)(NTP)$^{2-}$ and (ii) for the M(bpy)-(ATP)$^{2-}$ complexes the studies in solution[56] and in the solid state[57] agree that the formation of the intramolecular stack is connected with the release of N-7 from the coordination sphere of the metal ion.

5. Release of N-7 from the Coordination Sphere of the Metal Ion by the Formation of M(ATP)(OH)$^{3-}$. The fact that mixed-ligand complex formation with 2,2′-bipyridyl releases N-7 from the coordination sphere of the metal ion has prompted us to study this problem also for a ligand that cannot undergo a stacking interaction with the purine moiety. It seems of interest, also regarding biological systems, to know if this release is generally to be expected. The simplest ligand for studying this problem seemed to us OH^-.

As the macrochelated isomers of monomeric Cd(ATP)$^{2-}$ and Zn(ATP)$^{2-}$ reveal their presence clearly in ^{1}H NMR shift experiments,[19] we have now measured the chemical shifts of H-2, H-8, and H-1′ of 5 × 10^{-3} M 1:1 mixtures of Cd^{2+} or Zn^{2+}/ATP in D_2O as a function of "pH".[58] Under these conditions at pD 7.2 about 85% of Cd(ATP)$^{2-}$ and Zn(ATP)$^{2-}$ exists in the monomeric form.[59] This dependence of the chemical shifts is compared in Figure 2 with the distribution of the complex species, also as a function of pH, for the Cd^{2+}/ATP (upper part) and Zn^{2+}/ATP systems (lower part).

First of all, the chemical shifts of ATP change as expected with pH: the interaction of Cd^{2+} with N-7 (section 3) leads to the expected downfield shift of H-8, compared with the shift position in free ATP. The corresponding shift of H-2 is upfield, which is probably due to the known Cd^{2+}-promoted self-association,[19] while the shift of H-1′ remains rather uninfluenced by the coordination of Cd^{2+} to the adenine moiety. The chemical shifts, especially of H-2, in the lower pH region seem best to be explained by the sum of the concentrations of Cd(H·ATP)$^-$ and Cd(ATP)$^{2-}$; this suggests that not only in Cd(ATP)$^{2-}$ but also in Cd(H·ATP)$^-$ a Cd^{2+}/N-7 interaction exists. As the proton in Cd(H·ATP)$^-$ is apparently mainly located at the γ-phosphate group and not at N-1 (see section 2), such a macrochelation seems quite feasible.

However, the important result of Figure 2 is that with the increasing concentration of Cd(ATP)(OH)$^{3-}$ the shifts of H-2 and H-8 move back to the position in free ATP. This shows that hydroxo complex formation releases N-7 from the coordination sphere of Cd^{2+}. Moreover, as the formation degree of Cd(ATP)$^{2-}$ reaches more than 90% (upper part), the value of the acidity constant $pK^H_{Cd(ATP)(H_2O)}$ may be read directly from the shifts of H-2 and H-8: the result, $pK^H_{Cd(ATP)(H_2O)} \simeq 10.2$ (expressed in "pH"),[58] is in excellent agreement with

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(58) The expression "pH" represents the direct pH meter reading for a D_2O solution. The expression pD means that the following correction was applied:[28] pD = pH meter reading + 0.40. As the difference between pK_A values determined in H_2O and D_2O corresponds approximately to the given correction (see section 1), it is realistic to compare experiments carried out in H_2O and D_2O on the basis of the direct pH meter reading. See also footnote 11 in ref 37.

(59) The calculations with K = 17 M^{-1} (see Table II in ref 19) give for $[Cd^{2+}]_{tot} = [ATP]_{tot} = 5 \times 10^{-3}$ M: 85.9% monomer, 12.5% dimer, 1.4% trimer, 0.13% tetramer. The calculations with K_D^* = 20 M^{-1} and K_{st} = 4 M^{-1} (see legend of Figure 5 in ref 19) give for the mentioned conditions: 85.1% monomer, 14.5% dimer, 0.37% trimer, 0.04% tetramer. The corresponding calculation for Zn^{2+} under the same conditions gives 85–90% of the monomer.

the value of 10.1 from the potentiometric pH titrations (Table II; section 2), thus confirming that the alterations of the shifts are coupled with the formation of $Cd(ATP)(OH)^{3-}$.

The alterations of the chemical shifts produced by the coordination of Zn^{2+} to ATP are less pronounced than those obtained with Cd^{2+}; this agrees with earlier observations.[19] However, it is still evident that all the conclusions outlined above for Cd^{2+}/ATP are also valid for Zn^{2+}/ATP; especially, the release of N-7 from the coordination sphere of Zn^{2+} by the formation of $Zn(ATP)(OH)^{3-}$ is clearly seen. This release occurs at a pH that is about 1.3 log units lower than in the Cd^{2+}/ATP system, a result in excellent agreement with $pK^{H}_{Zn(ATP)(H_2O)} = 8.87$ (ref 41) and $pK^{H}_{Cd(ATP)(H_2O)} = 10.1$ (Table II).

Hence, the formation of the simple mixed-ligand complex $M(ATP)(OH)^{3-}$ is connected with the release of N-7 from the coordination sphere of the metal ion and therefore also with the opening of the macrochelate. Consequently, it seems possible that the formation of mixed-ligand complexes is usually always connected with the disappearance of the macrochelated isomer.

Conclusions

The results show that the coordinating properties of Cd^{2+} and Zn^{2+} with regard to nucleotides are similar and that ATP^{4-} is a very versatile ligand. The complex $M(ATP)^{2-}$ may exist at least in two isomeric forms: (i) the metal ion may only be coordinated to the phosphate chain or (ii) the metal ion may in addition interact with the base residue. This contrasts with the $M(CTP)^{2-}$ complexes, which exist only in the phosphate-coordinated form.

Considering that ATP participates in enzymic reactions usually in the form of $M(ATP)^{2-}$, these different structures may be of biological relevance. Important also in this connection is the indication, obtained from the present studies with Zn^{2+} and Cd^{2+}, that formation of mixed-ligand complexes leads to the release of N-7 from the coordination sphere of the metal ion, and hence a structural rearrangement is in this way initiated.

The described observations, together with the metal ion promoted self-association of ATP[19] and its ability to interact in an intramolecular fashion via hydrophobic and stacking interactions with the second ligand in mixed-ligand complexes,[35,51] show that ATP is a ligand suitable to satisfy many demands regarding specificity. CTP is in this respect a much less versatile ligand. Obviously, nature is making use of these differences, as well as of all the possibilities inherent in the ATP molecule.

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Preparation, Characterization, and Outer-Sphere Electron-Transfer Reactions of Nickel Complexes of 1,4,7-Triazacyclononane

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An unusually stable nickel(III) complex ion, $[Ni(1,4,7\text{-triazacyclononane})_2]^{3+}$, is described. Modification of an existing procedure leads to good yields of the ligand trihydrochloride. The nickel(III) complex has been prepared via oxidation of the nickel(II) analogue reported previously. The octahedral NiN_6 configuration is retained on electron transfer, and outer-sphere reactions have been studied. In the oxidation of iodide, under conditions of $[I^-]$ up to 80-fold in excess over oxidant, the rate law may be written as $R = k_6[Ni(III)][I^-]$ with $k_6 = 191\ M^{-1}\cdot s^{-1}$. A similar first-order dependence is observed in the oxidation of $Co(phen)_3^{2+}$ ($k_5 = 5.6 \times 10^5\ M^{-1}\cdot s^{-1}$). A self-exchange rate for the Ni(III/II) couple of $6.0 \times 10^3\ M^{-1}\cdot s^{-1}$ has been evaluated by using a Marcus correlation. The system represents one of the few examples where outer-sphere reaction pathways of Co^{3+} and $CoOH^{2+}$ may be assigned. The observed rate constant for the reaction of Co^{3+} + $Ni(nonaneN_3)_2^{2+}$ ($k_3 = 430\ M^{-1}\cdot s^{-1}$) is in good agreement with that predicted ($370\ M^{-1}\cdot s^{-1}$) by using recent data for the $Co^{3+/2+}$ exchange. Estimates are presented for the $CoOH^{2+/+}$ exchange rate.

Introduction

The oxidation of nickel(II) amine complexes in aqueous solution has been studied extensively over the past few years,[1,2] and the existence of this metal center in both the trivalent[3,4] and tetravalent[2,5] states has now been well documented. Since the nickel(III) complexes are conveniently generated by oxidation of the corresponding nickel(II) amines and because the higher valent ions are in aqueous media generally only kinetically stable to any extent only under acidic conditions ($[H^+] > 0.1$ M), studies have centered mainly on those compounds that are stable in acid. This criterion is well met by the tetraaza macrocyclic complexes of nickel(II).[6-8] In contrast, studies with ethylenediamine as ligand provide evidence for $Ni(en)_3^{3+}$ as having only transitory existence.[9] Only

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