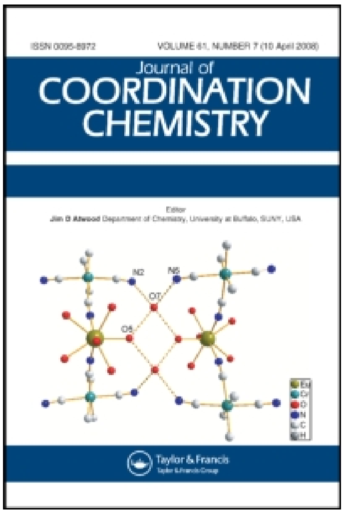

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THE AFFINITY OF THE VANADYL(IV) ION FOR NITROGEN DONOR LIGANDS

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The affinity of the VO^{2+} ion for nitrogen donor ligands is discussed in terms of predictions made previously. A dual basicity equation predicts $\log K_1(NH_3) = 3.0$ for VO^{2+}. Equations that model the chelate effect are used to show that this is a reasonable prediction. In accord with experience, the vanadyl ammines should be hydrolyzed in aqueous solution, as should also the ethylenediamine complexes. The formation constants of VO^{2+} with a variety of more hydrolysis-resistant chelating nitrogen donor ligands, 2,2′-bipyridyl, 1,10-phenathroline, *o*-aminomethyl-pyridine, 2-(2-pyridyl)-imidazole, *N,N,N′,N′*-tetrakis(2-hydroxypropyl)ethylenediamine, di-2-pyridyl-amine, 2,2′,2″-terpyridyl, and picolinic acid, are reported, determined by glass electrode potentiometry. It is shown that these formation constants are consistent with the predicted $\log K_1(NH_3)$ for VO^{2+}, supporting the validity of the dual basicity equation use.

KEYWORDS: Vanadyl, nitrogen donors, stability constants

INTRODUCTION

Acid-base interactions are a subject of enduring interest.[1] We have attempted[2–4] to understand the general principles controlling acid-base interactions in aqueous solution, which are important for metal-ligand interactions in biomedical applications, including imaging agents,[5] cancer therapy,[6] and analgesics.[7] A unifying principle in acid-base studies has been the Hard and Soft Acids and Bases (HSAB) principle of Pearson,[8] coupled with the dual-parameter ‘E and C’ equation of Drago and Wayland.[9] In 1978 a dual basicity equation[2] (*1*) similar to the E and C equation was used to analyze acid base interactions in aqueous solution.

$$\log K_1 = E_A^{aq} \cdot E_B^{aq} + C_A^{aq} \cdot C_B^{aq} \qquad (1)$$

In this equation, E and C are the tendency toward ionic and covalent bonding on the part of the acid (subscript ‘A’) or base (subscript ‘B’). The superscript ‘aq’ distinguishes these parameters from those of Drago and Wayland, which apply in solvents of low dielectric constant. The E and C parameters are empirically derived in a manner analogous to those of Drago and Wayland. It was necessary[3] in some cases to add a third pair of parameters to the basic two-pair system employed by Wayland and Drago to account for steric effects where the donor atom of the

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incoming ligand was much larger than the water displaced on complex formation. For ligands such as OH^-, NH_3 and F^- this is not necessary, and equation (*1*) can be used as it stands to correlate $\log K_1$ values for complexes F^-, OH^-, and NH_3.

In spite of the success of (*1*), where all known $\log K_1$ values for these complexes could be predicted to within 0.2 log units, this equation has received little attention. This may be because the validity of an empirical equation remains doubtful until it has made successful predictions of data not included in the fitting of its parameters. The predictions should preferably be for data rather different from those used for fitting the equation, and be for results that would not have been routinely expected. In order to test the reliability of (*1*), we have embarked on a program of checking its predictions. The formation constants of the F^- and OH^- complexes of most metal ions are known,[10] so it is the predictions of unknown $\log K_1(NH_3)$ values that must be checked.

Equation (*1*) can be rearranged, substituting in appropriate E and C parameters, so that $\log K_1$ values for NH_3 complexes can be directly predicted from the $\log K_1$ values for F^- and OH^- complexes:

$$\log K_1(NH_3) = 0.881 \log K_1(OH^-) - 1.08 \log K_1(F^-) \qquad (2)$$

A problem here is that for most metal ions, the ammine complexes decompose in water according to equations of the type:

$$M(NH_3)^{n+} + H_2O = MOH^{(n-1)+} + NH_4^+ \qquad (3)$$

Predictions of equation (*2*) for these metal ions can thus not be directly verified. However, all values of $\log K_1(NH_3)$ predicted by equation (*2*) are consistent with the non-existence of these ammines in aqueous solution according to equation (*3*). One way of obtaining[11] independent estimates of $\log K_1(NH_3)$ values for these metal ions has used the type of correlation seen in Figure 1. The assumption made here[11] is that the process of replacing a ligand such as ODA (see Figure 2 for key to ligand abbreviations) with IDA, which contains an N-donor in place of the O-donor of ODA, will resemble the process of formation of an ammine, where a coordinated water molecule is replaced by ammonia. A gratifying aspect of the predictions of correlations such as those in Figure 1 is that they agree well with the predictions of equation (*2*). A further method of estimating[12] $\log K_1(NH_3)$ values has involved chelate effect equations such as (*4*).

$$\log K_1(polyamine) = 1.152 \log\beta(NH_3) + (n-1)\log 55.5 \qquad (4)$$

This equation predicts $\log K_1$ values for polyamines such as TRIEN from known $\log\beta_n$ values for the ammines. The $(n-1)\log 55.5$ term is the entropic contribution to the chelate effect according to Adamson.[13] This equation has been extended[12] to include $\log K_1$ values for polyaminocarboxylates such as EDTA. Where $\log K_1$ values are known for a metal ion such as Bi^{3+} with EDTA and a variety of other polyaminocarboxylates, a value of $\log K_1(NH_3)$ may be estimated. Again, $\log K_1(NH_3)$ values estimated by this method agree with $\log K_1(NH_3)$ values estimated from equation (*2*) and from correlations such as Figure 1.

In order to test the validity of the above approaches to predicting and understanding the solution chemistry of metal ions, we have checked out such predictions for a variety of metal ions, including Pb(II),[11,14] the lanthanides,[15] the uranyl ion,[16] and Ga(III) and In(III).[17] Work in progress on Bi^{3+} using polarogra-

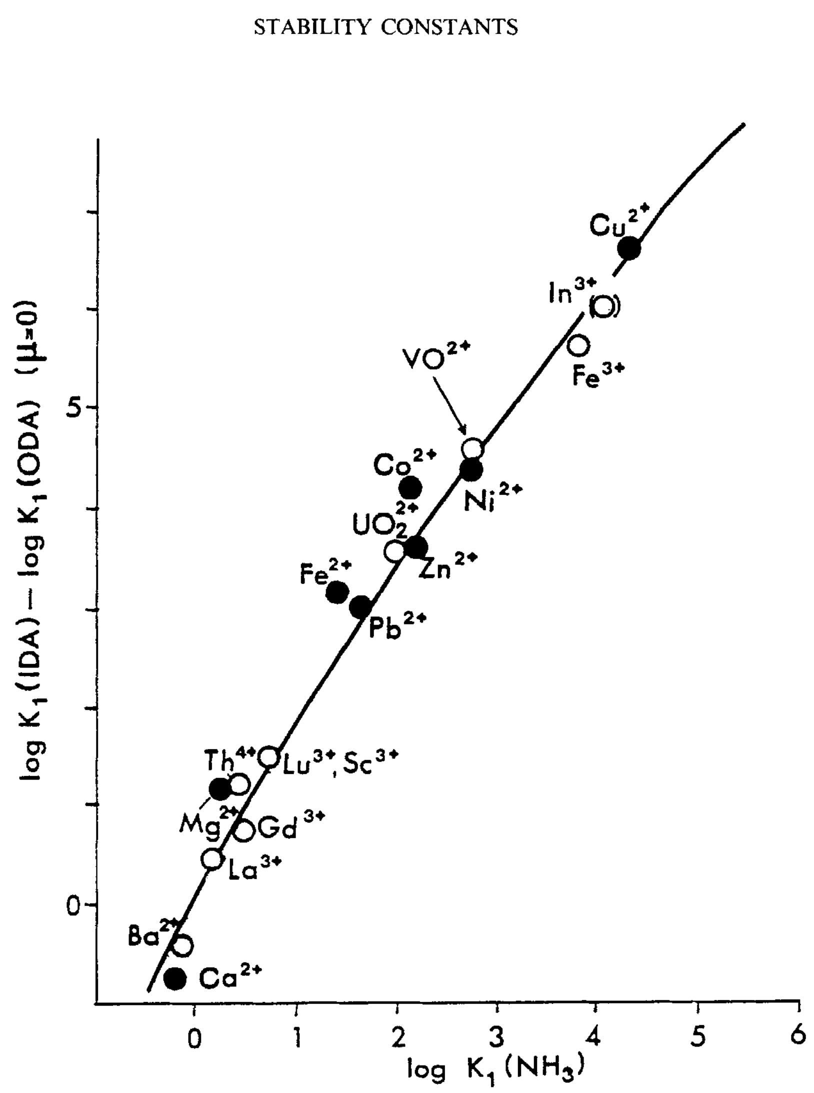

Figure 1 The relationship between $\log K_1$ (IDA)-$\log K_1$(ODA) and $\log K_1$ (NH_3) for a variety of metal ions. The filled circles are for metal ions where $\log K_1$ (NH_3) is known[10] experimentally, while open circles estimate $\log K_1$ (NH_3) values estimated as discussed in the text. Formation constants are from reference 10, with the values for VO^{2+} having become available only since this diagram was first published.[11]

phy to allow for the study of complex formation by amines in strong acid, and at very low Bi concentrations to prevent precipitation of bismuth hydroxide, has shown a chemistry with amine ligands in good agreement with predictions.[18]

Here we consider the vanadyl ion. From $\log K_1(F^-) = 3.98$ and $\log K_1(OH^-) = 8.3$ at infinite dilution,[10] (*2*) predicts $\log K_1(NH_3)$ for the VO^{2+} ion of 3.0. The correlation in Figure 1 indicates that $\log K_1(NH_3)$ will be 2.7 for the vanadyl ion, in reasonable agreement. Since the only reported[10] value for $\log K_1(F^-)$ with VO^{2+} is at an ionic strength of 1.0, our correction of this to infinite dilution may be a little

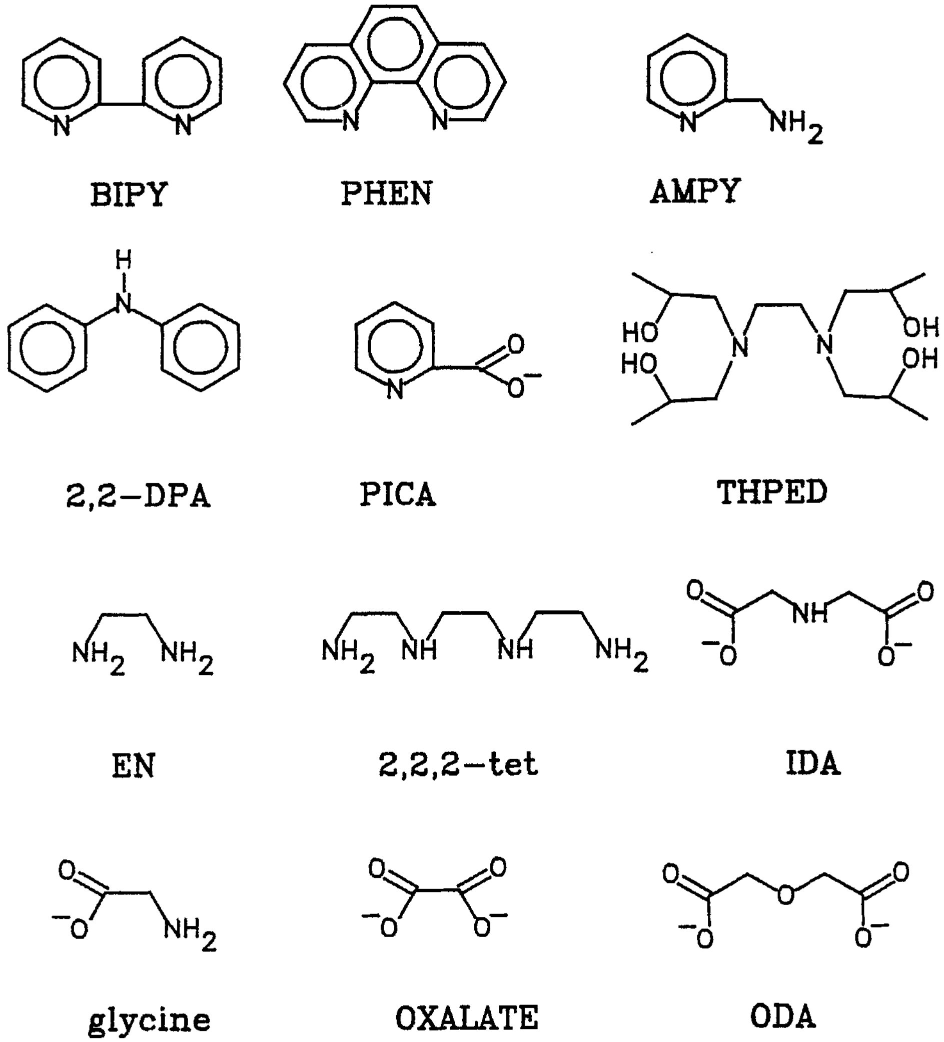

Figure 2 Ligands discussed in this paper.

inaccurate, and for this reason the predicted value of $\log K_1(NH_3) = 3.0$ from (*2*) may be regarded as less reliable than the 2.7 obtained from Figure 1, so that the value of $\log K_1(NH_3) = 2.7$ for VO^{2+} will be preferred here. Including the known[10] formation constants and solubility products for VO^{2+} hydroxides in species distribution calculations shows that ammonia complexes of VO^{2+} will be totally hydrolyzed in aqueous solution with a $\log K_1(NH_3)$ of 2.7 (or even 3.0). Use of equation (*4*) predicts $\log K_1(EN) = 7.5$, and this complex should also be totally hydrolyzed. Reported[19] complexes of VO^{2+} with EN in aqueous solution therefore require checking. The types of amines which can be used[11–18] to limit hydrolysis according to equation (*3*) are those where the protonation constants of the ligand are lowered by use of pyridyl donor groups or *N*-hydroxyalkyl groups, which has a relatively smaller effect on the formation constants of the metal ion with the ligand. In this paper we report a glass electrode study of the formation constants of the vanadyl ion with pyridyl containing ligands BIPY, AMPY, 2,2-DPA, PHEN, PICA and PYR-Im, and the hydroxyalkyl-containing ligand THPED. A study of VO^{2+} complexation by 2,2,2-tet and EN was also attempted.

EXPERIMENTAL

Materials

The ligands AMPY and BIPY were obtained from Aldrich, THPED and PICA from BDH, and EN and 2,2,2-tet from Merck. PYR-Im was a gift of Dr B. Green of MINTEK. Vanadyl sulfate trihydrate (99.99%) was obtained from Aldrich. The ligands were standardized by titration with acid, which indicated that they were all better than 99% pure. A stock solution of approximately 0.01 M vanadyl sulfate in 0.1 M $NaNO_3$ was prepared.

Potentiometry

Titrations were carried out under nitrogen in a cell thermostatted to 25°C in 0.1 M $NaNO_3$, using a Radiometer G202B glass electrode, and Radiometer PHM 84 pH meter. The standard potential for the cell, E°, was obtained from calculated values of pH in the range of pH values from 2 to 12 in a standard acid/base titration. At least three titrations with variation of metal/ligand ratio were performed for each ligand with vanadyl ion.

Analysis of potentiometric data

The potentiometric titrations were analyzed using the program ESTA.[20] A large number of possible solution species were considered, of the type $M_aL_bH_c(OH)_d$, with a wide range of values for a, b, c, and d. To account for hydrolysis, the appropriate literature[10] values for the hydroxy complexes of VO^{2+} and the solubility product of $VO(OH)_2(s)$, shown in Table 1, were included in the calculations using ESTA.

In Figures 3–6 are seen the $\bar{z}$ *versus* log[L] plots for a selection of the complexes studied here, showing both the experimental points, and theoretical curves calculated from the constants in Table 1. The function $\bar{z}$ is[20] $\{L_T - j^{-1}(H_T - [H] - K_W[H]^{-1})\}$ where L_T is the total ligand concentration, j is $\{\beta_1[H] + 2\beta_2[H]^2 + \ldots\} / (1 + \{\beta_1[H] + 2\beta_2[H]^2 + \ldots)$, H_T is the total proton concentration, and M_T is the total metal concentration. The function $-\log[A]$ in these plots refers to $A = (H_T - [H] + K_w \cdot [H]^{-1})/(\{\beta_1[H] + 2\beta_2[H]^2 + \ldots)$. The interpretation of the $\bar{z}$ *versus* log[A] plots is not too different from that of the more familiar n *versus* log[L] plots, except that the z plots facilitate[20] analysis of curves where species of composition other than ML_b are present.

Table 1 Formation constants for complexes of vanadyl, and protonation constants, with a variety of ligands.[a]

Ligand[b]	Equilibrium	log of formation constant[c]
OH^-	$H^+ + OH^- = H_2O$	13.78[d]
	$VO^{2+} + OH^- = VO(OH)^+$	7.9[d]
	$2VO^{2+} + 2OH^- = VO_2(OH)_2^{2+}$	28.35[d]
	$VO^{2+} + 2OH^- = VO(OH)_2$	18.31[d]
	$VO^{2+} + 2OH^- = VO(OH)_2(s)$	-23.5[d]
AMPY	$L + H^+ = LH^+$	8.61[d]
	$LH^+ + H^+ = LH_2^{2+}$	2.00[d]
	$VO^{2+} + L = VOL^{2+}$	6.75(2)
	$VOL^{2+} + L = VOL_2{}^{2+}$	5.29(2)
BIPY	$L + H^+ = LH^+$	4.42[d]
	$VO^{2+} + L = VOL^{2+}$	5.08(3)
	$VOL^{2+} + L = VOL_2^{2+}$	3.57(3)
	$VOL^{2+} + OH^- = VOL_2(OH)^+$	1.23(3)
2,2′-DPA	$L + H^+ = LH^+$	7.14[d]
	$VO^{2+} + L = VOL^{2+}$	5.48(3)
	$VOL^{2+} + L = VOL_2^{2+}$	3.89(3)
	$VOL_2^{2+} + L = VOL_3^{2+}$	2.45(5)
O-PHEN	$L + H^+ = LH^+$	4.93[d]
	$VO^{2+} + L = VOL^{2+}$	5.48(4)
	$VOL^{2+} + L = VOL_2^{2+}$	4.77(3)
	$VOL^{2+} + OH^- = VOL_2(OH)^+$	5.12(4)
PICA	$L + H^+ = LH^+$	5.21[d]
	$LH^+ + H^+ = LH_2{}^{2+}$	1.0[d]
	$VOL^{2+} + L = VOL^{2+}$	6.68(3)
	$VOL^{2+} + L = VOL_2{}^{2+}$	5.31(2)
PyrIm	$L + H^+ = LH^+$	5.47[d]
	$VO^{2+} + L = VOL^{2+}$	4.92(1)
	$VOL^{2+} + L = VOL_2{}^{2+}$	4.56(1)
	$VOL^{2+} + OH^- = VOL_2(OH)^+$	4.12(2)
THPED	$L + H^+ = LH^+$	8.75[d]
	$LH^+ + H^+ = LH_2{}^{2+}$	4.24[d]
	$VO^{2+} + L = VOL^{2+}$ ML	6.57(3)
2,2,2-terpy	$L + H^+ = LH^+$	4.65[d]
	$LH^+ + H^+ = LH_2{}^{2+}$	3.5[d]
	$VO^{2+} + L = VOL^{2+}$ ML	6.40(3)
	$VOL^{2+} + L = VOL_2{}^{2+}$	9.26(4)

[a] Formation constants this work, at 25°C and in 0.1 M $NaNO_3$, except where otherwise indicated. [b] For key to ligand abbreviations, see Figure 2. [c] The number in parentheses after each formation constant indicates the standard deviation indicated by the program ESTA.[20] [d] Constants from reference 10.

RESULTS AND DISCUSSION

The formation constants obtained for vanadyl are seen in Table 1. The significance of Table 1 is that, in accord with expectations in the discussion, the VO^{2+} ion does have a considerable aqueous phase chemistry with nitrogen donor ligands, provided these are stabilized against hydrolysis by the presence of pyridyl donors or hydroxyalkyl groups on the saturated nitrogen donors. The test of the ideas promoted here must lie in the extent to which the chemistry of VO^{2+} accords with expectations based on these ideas. For metal ions of reasonably short M-N bond length, *i.e.*, in the vicinity of 2.0 Å, addition of 2-hydroxyalkyl groups results in a

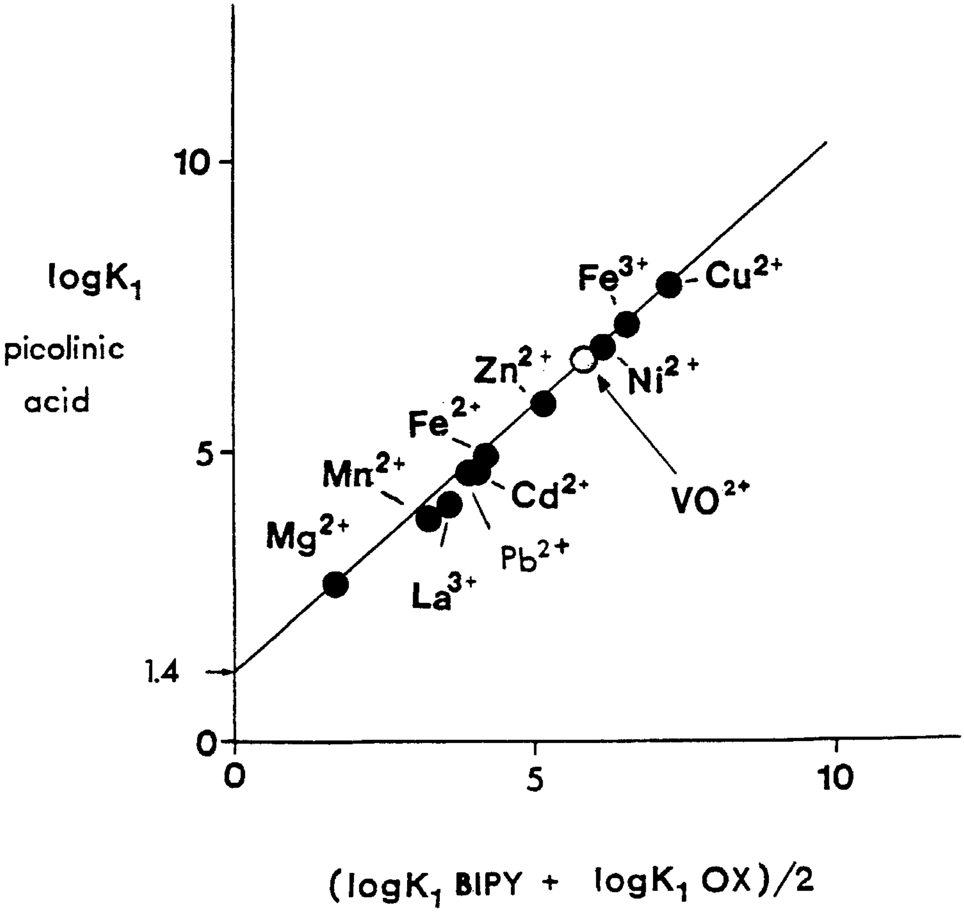

Figure 3 The rule of average environment[21] as shown in modified form by the set of ligands picolinic acid, BIPY (2,2′-bipyridyl) and OX (oxalate). The point for VO^{2+} is shown as an open circle to highlight how well the $\log K_1$ values for this ion, determined in this work, fit the rule. The rule is obeyed in an unusual way here with the observation of an intercept in the correlation.

modest decrease in $\log K_1$, which would appear to be expected from the V-N bond lengths reported[21] for a complex of VO^{2+} with 9-aneN_3. Thus, $\log K_1$ (THPED) = 6.57 found here for VO^{2+} supports the idea that it has a reasonably large $\log K_1$ with EN, and hence from (*4*), for ammonia:

Metal Ion	$\log K_1$(EN)	$\log K_1$(THPED)
Cu(II)	10.7	9.8
Ni(II)	7.5	7.5
Zn(II)	5.9	6.1
VO^{2+}	(7.5)	6.57

(logK_1 values from ref. 10, except for VO^{2+} with THPED, which is from this work, and EN, which was estimated as discussed in the text).

The value of logK_1 (THPED) for VO^{2+} may be marginally lower than anticipated, which may reflect the oxo group blocking coordination of, or interfering sterically with, one of the 2-hydroxypropyl groups of THPED. However, if we consider that from the estimated logK_1 (EN) = 7.5, we would have predicted logK_1 (THPED) close to 7.0 for VO^{2+}, an observed logK_1 (THPED) = 6.57 is quite reasonable.

We can use the *rule of average environment*[21] to analyze the affinity for saturated nitrogen donor ligands such as EN. This rule states that for simple bidentate ligands the formation constant of a ligand that contains two different donor groups will be the average of those for the ligands each containing only one of the two types of donor group. Thus, logK_1 for glycine complexes is close to the average of logK_1 for EN and oxalate complexes of the same metal ion. Similarly, logK_1 for AMPY complexes is close to the mean for the corresponding BIPY and EN complexes:

Metal Ion	logK_1 (BIPY)	logK_1 (EN)	logK_1 (AMPY)	
			calc	obsd
Ni^{2+}	7.04	7.33	7.19	7.11
Mn^{2+}	2.62	2.67	2.65	2.66
Pb^{2+}	2.9	5.04	3.97	3.95
VO^{2+}	5.08	(7.5)	6.29	6.75

(Formation constants from ref. 10, except for VO^{2+}, this work (AMPY and BIPY), and estimated as described in the text (EN)). Again the level of agreement between logK_1 (AMPY) calculated from the rule of average environment, and observed, is reasonable. The value of logK_1 (BIPY) = 5.08 also illustrates the use of the rule with logK_1 (ox) = 6.79 (ref. 10, but corrected to ionic strength 0.1 by comparison with M^{2+} ions where logK_1 is known at several ionic strengths) for VO^{2+}. The complexes of PICA do not follow the rule in its simplest form.[21,22] Rather, a relationship such as seen in Figure 3 is obtained, where the intercept is thought[22] to reflect lower steric problems from the *ortho* hydrogens on the pyridyl groups in the complexes with PICA than with BIPY. Figure 3 shows how well the measured value of logK_1 (PICA) with VO^{2+} fits in with ideas on complex formation discussed here. A third type of correlation[14] for nitrogen donor ligands is seen for BIPY and NH_3 in Figure 4. Here again the estimate of logK_1(NH_3) of 2.7 for VO^{2+} is seen to be reasonable in terms of the correlation. Similar correlations are obtained for other ligands studied here, such as 2,2′-DPA and pyr-IM.

A question that arises here is just how important these amine complexes are as solution species. As shown in Figure 5, the species distribution diagram for VO^{2+} complexes with PyrIm, the amine-containing species are the dominant species in solution, with more or less complete suppression of hydroxy species up to the point of precipitation above pH 6. Titrations with EN and VO^{2+} revealed no species other than hydroxy species in solution. Titrations with 2,2,2-tet were interesting. In titrating VO^{2+}/2,2,2-tet solutions, a precipitate formed at around pH 3.5, which appeared to be $VO(OH)_2(s)$. This then redissolved at about pH 5, with reprecipitation occurring at about pH 10. We may offer a tentative analysis of this phenomenon. Equation (*4*) predicts logK_1 (2,2,2-tet) = 14.7 from logK_1 (NH_3) = 2.7

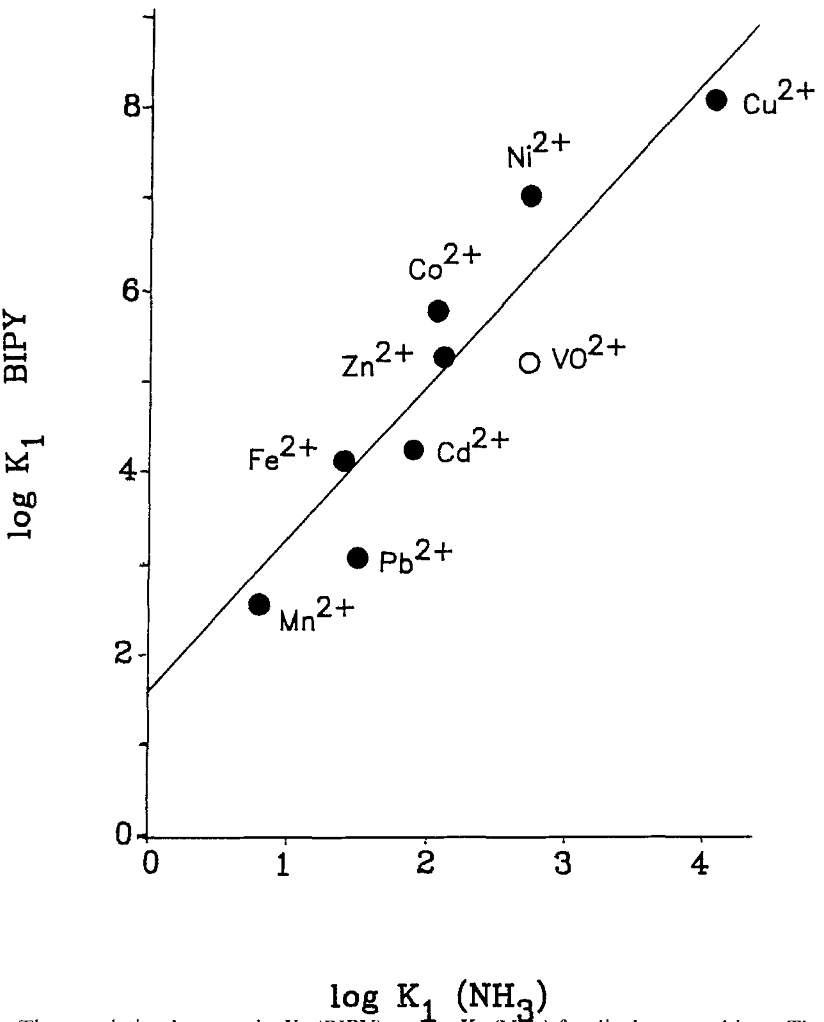

Figure 4 The correlation between $\log K_1$ (BIPY) and $\log K_1$ (NH_3) for divalent metal ions. The open circle for VO^{2+} shows that the estimated $\log K_1$ (NH_3) value for this ion is reasonable. Data are from reference 10, except for $\log K_1$ (BIPY) for VO^{2+}, which is from this work.

for VO^{2+}. Calculation of a species distribution diagram for VO^{2+} with 2,2,2-tet, using this estimate for $\log K_1$ (2,2,2-tet), and including hydroxy species, gives Figure 6. Figure 6 shows that $VO(OH)_2(s)$ will precipitate at pH 3.5. This will then redissolve to form the $[VO(2,2,2\text{-tet})]^{2+}$ complex at pH 5, which will persist in solution all the way up to pH 10, when the hydroxide will reprecipitate. This initially suprising phenomenon results because the formation of $[VO(2,2,2\text{-tet})]^{2+}$ has a fourth power dependency on proton concentration, derived from deprotonating 2,2,2-tet, whereas formation of $VO(OH)_2(s)$ involves only two protons. Thus, although we were not able to measure $\log K_1$ for 2,2,2-tet with VO^{2+}, the behaviour

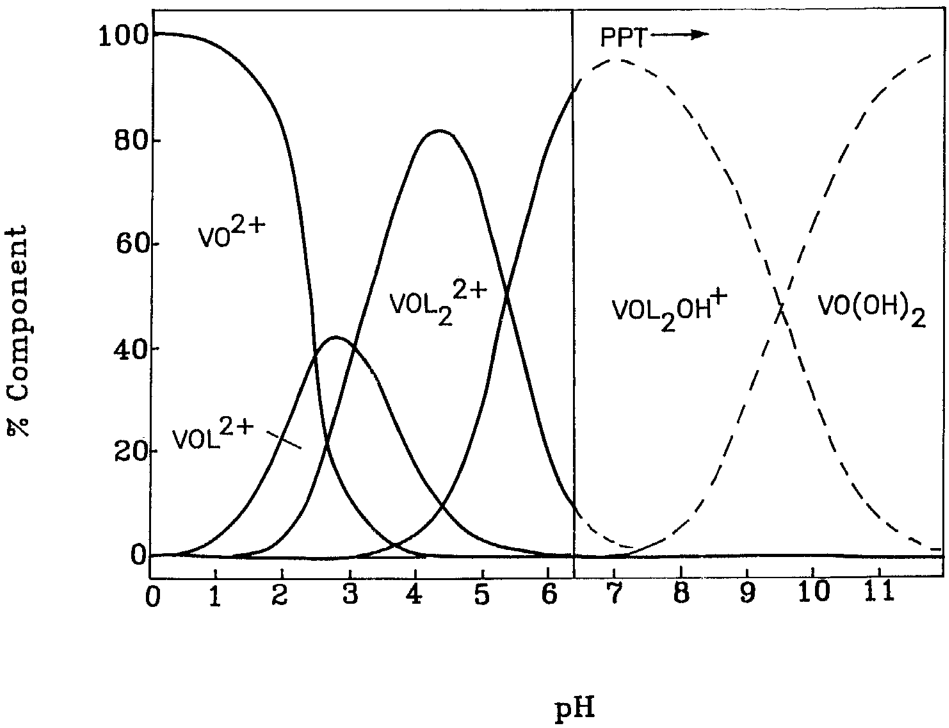

Figure 5 Species distribution diagram for VO^{2+} and L = Pyr-Im [2-(2-pyridyl)-imidazole] as a function of pH, calculated with total $VO^{2+} = 2 \times 10^{-3}$ M and total pyr-Im = 10^{-2} M. The solid vertical line at pH = 6.4 indicates the point at which a precipitate (PPT) of $VO(OH)_2(s)$ begins to form.

observed in the titrations is consistent with the $\log K_1$ predicted by equation (*4*). What is needed is to use a technique for studying the VO^{2+}/2,2,2-tet system at total vanadium concentration of less than 10^{-6} M to prevent precipitation of $VO(OH)_2(s)$, as is available for Bi(III) complexes with polarography.

In summary, it seems that the chemistry of VO^{2+} with nitrogen donor ligands in aqueous solution accords reasonably well with predictions based on earlier ideas. How this has worked out for the metal ions considered so far is seen below:

Metal ion	Mean $\log K_1$ (NH_3) predicted by approaches of the type			
	equation 1	equation 4	Figure 1	Figure 4
VO^{2+}	3.0	2.7	2.7	2.3
UO_2^{2+}	2.0		2.0	
In^{3+}	4.0	4.0	4.0	4.0
Ga^{3+}	4.1	4.1		4.1
Bi^{3+}	5.0	5.0	4.4	4.2
Pb^{2+}	2.1	1.6	1.6	1.3
La^{3+}	0.4	0.2	0.2	0.2
Lu^{3+}	0.7	0.7	0.7	

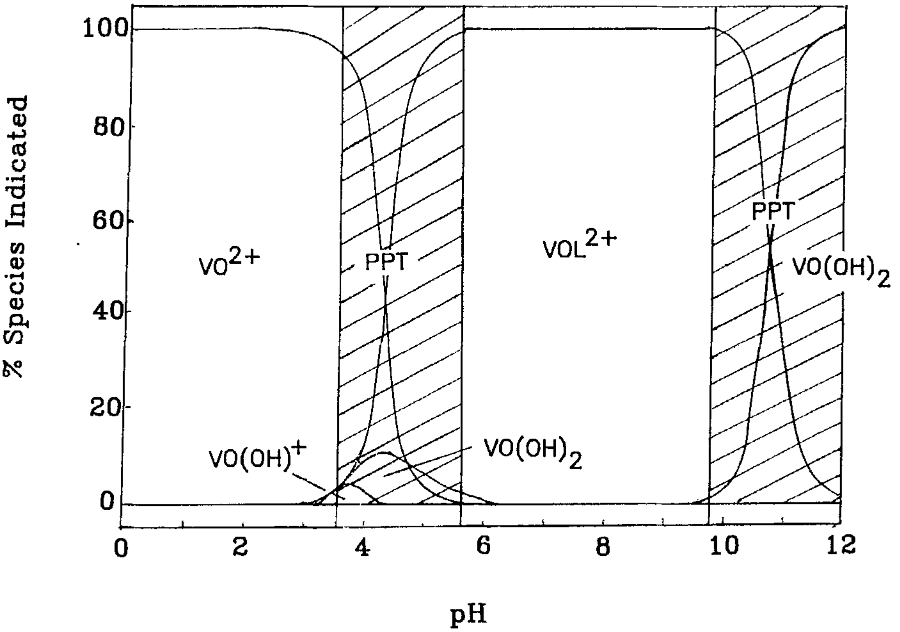

Figure 6 Species distribution diagram for VO^{2+} and L = 2,2,2-tet (1,4,7,10-tetrazadecane) as a function of pH, calculated with total VO^{2+} = 2×10^{-3} M and total 2,2,2-tet = 10^{-2} M. The calculation was carried out with $\log K_1$ (2,2,2-tet) = 14.7 for VO^{2+}, estimated as described in the text. The solid vertical line at pH = 3.5 indicates the point at which a precipitate (PPT) of $VO(OH)_2(s)$ begins to form, while the second vertical line at pH 5.6 indicates where the precipitate will redissolve, precipitating again at pH 9.7.

It appears that the level of agreement that is building up between these different methods of predicting or assessing the stability of ammine complexes of these highly acidic metal ions is such that one may, in particular, regard equation (*1*) and the E^{aq} and C^{aq} parameters that we have developed as a reasonable model of Lewis acid-base interaction in aqueous solution, and use it as a guide in efforts aimed at designing better ligands. This is particularly so since equation (*1*) refers to water, the most important solvent, and should give insights into acid-base behaviour in biological systems.

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