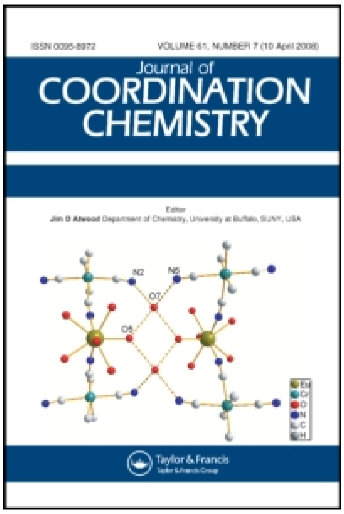

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OXOVANADIUM(IV) COMPLEXES OF DI- AND TRIPHOSPHATE

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OXOVANADIUM(IV) COMPLEXES OF DI- AND TRIPHOSPHATE

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The interaction of oxovanadium(IV) ion with diphosphoric and triphosphoric acids in aqueous solution was investigated over the measurable pH range by means of potentiometry, electronic absorption and EPR measurements. The results show that both diphosphate and triphosphate, partially or fully deprotonated depending on pH, are able to chelate the metal ion to yield several mononuclear species. With triphosphate, there is no evidence for the formation of a species analogous to the already reported and well-characterized trinuclear complex formed by diphosphate acting as a chelating and bridging ligand through the four unshared oxygen atoms.

KEYWORDS: oxovanadium(IV), trinuclear complexes, diphosphoric acid, triphosphoric acid, potentiometric studies, EPR.

INTRODUCTION

There is strong evidence that vanadium is an essential trace element and its biochemistry has been recently reviewed by Rehder.[1] Our interest in the interaction of oxovanadium(IV) with phosphate, diphosphate and triphosphate stems from these being, as part of more complex ligands inside the cell, preferential binding sites for the metal ion. The strong affinity of VO^{2+} primarily for phosphates has been assessed through the determination of the association constants of both V(IV), as VO^{2+}, and V(V), as VO_4^{3-}, $HVO_4^{2-}$and $H_2VO_4^-$, with extra- and intra-cellular ligands.[2] Up to 70% of vanadium, which is present in the cell in concentrations of 10^{-7}–10^{-8} M, essentially as VO^{2+}, binds to phosphates such as ATP, ADP, AMP and inorganic phosphate. Further, creatine phosphate, if present, as in muscle cells in a 0.03 M concentration, is able to bind nearly 61% of total VO^{2+}. These

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interactions help stabilize the V(IV) oxidation state due to complex formation; *e.g.*, the trapping of VO^{2+} by the triphosphate moiety of ATP decreases the rate of oxidation of vanadyl ion to vanadate,[3] which is mainly responsible for vanadium poisoning.[4]

A spectrophotometric investigation of the interaction of the oxovanadium(IV) ion with diphosphate suggests the formation of a six-membered mono-chelated complex at pH 2 but higher pH ranges were not investigated.[5] EPR studies show that, in the pH range 5–9, complete deprotonation of the ligand allows the formation of a trinuclear cyclic complex with a 1:1 $VO^{2+}:P_2O_7^{4-}$ stoichiometry.[6–8] This species is characterized by an isotropic EPR spectrum in which 22 hyperfine lines are detected. The trimetallic system dissociates above pH 9 and the formation of a mononuclear bis-chelated complex follows.[6] The latter does not prevent VO^{2+} from being hydrolyzed at pH 11.

The only available data concerning the triphosphate-VO^{2+} system in aqueous solution were obtained by a potentiometric investigation of the pH interval 2.5–6.5 with ligand-to-metal molar ratios ranging from 1.5 to 3.[9] Thermodynamic results suggest that triphosphate complexes are more stable than those formed by phosphate and diphosphate but only two species, $[VO(HP_3O_{10})]^{2-}$ and $[VO(P_3O_{10})]^{3-}$, were detected. As a matter of fact, a detailed spectroscopic and potentiometric analysis of this system is lacking.

We have reconsidered both systems and have investigated larger pH ranges by means of potentiometric titrations, EPR and electronic absorption spectroscopy.

EXPERIMENTAL

The ligands were Aldrich products of the highest available quality, used without further purification. The purity of the ligands was checked and the exact concentration of their solutions was determined by the Gran method.[10] A VO^{2+} stock solution[11] was standardised for metal concentration by permanganate titration and for hydrogen ion concentration by potentiometry using the appropriate Gran function. The ionic strength was adjusted to 0.2 M with KCl. In all cases, the temperature was 25 °C.

Stability constants of the proton and the oxovanadium(IV) complexes were determined by pH-metric titration of 25.0 cm^3 samples. The ligand concentration was 0.004 and 0.002 M and the ligand-to-metal ion molar ratio 8:1, 6:1, 4:1, 2:1 and 1:1. The titrations were performed over the pH range 2–10, or until precipitation occurred, with KOH solution of known concentration (*ca* 0.2 M) under a purified argon atmosphere. When 10 minutes were not enough to reach pH equilibrium, titration points were omitted from data evaluation.

The pH was measured with a Radiometer pHM 84 instrument, and a GK 2322C combined electrode, calibrated for hydrogen ion concentration according to Irving *et al.*[12] The difference between pH meter readings and $-\log[H^+]$ was constant in the pH range 2–4 and 10–11.6. Thus the junction potential proved to be constant, although not negligible, as discussed in detail previously.[12] Concentration stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^qH^r$ were calculated with the aid the PSEQUAD computer program.[13] Equilibria corresponding to the formation of the hydroxo complexes of VO(IV) were taken into account in the calculation of the stability constants of the complexes. The following species were assumed: $[VO(OH)]^+$ (log

$\beta_{1-1} = -5.94$), $[\{VO(OH)\}_2]^{2+}$ (log $\beta_{2-2} = -6.95$), with stability data calculated from the data published by Henry *et al.*[14] and corrected for the different ionic strengths by use of the Davis equation, and $[VO(OH)_3]^-$ (log $\beta_{1-3} = -18.0$), taken from ref. 15.

Isotropic and anisotropic X-band EPR spectra (9.15 GHz) were recorded at 298 or 140 K, respectively, on aqueous systems using a Varian E-9 spectrometer. As usual, the samples for low-temperature measurements were mixed with a few drops of DMSO to ensure good glass formation in frozen solutions. Absorption spectra were obtained on a Beckman Acta MIV spectrophotometer.

RESULTS AND DISCUSSION

Diphosphoric acid, $H_4P_2O_7$, has a very acidic proton ($pK_a < 1$) while pK_a values for the dissociation of the other protons are 1.66, 5.88 and 8.25, respectively. These data are in reasonable good agreement with those measured earlier under similar experimental conditions, especially if the significant ionic strength dependence of the acidity constants of this highly charged molecule is also taken into account; pK values reported earlier are 1.97, 6.03 and 8.40 at I = 0.1 M, and 1.85, 5.63 and 7.87 at I = 0.5 M.[16] With the exception of pK_{a2}, our values determined at I = 0.2 M lie between the two sets of data.

EPR measurements were used to follow metal complexation in the VO(IV)-diphosphate system. Representative isotropic EPR spectra of a $[VO^{2+}] = 0.1$ M aqueous solution with equimolar diphosphate ligand are shown in Figure 1. Even below pH 2 the spectroscopic features are different from those of the aqua ion, the line width is greater and the magnetic parameters measured at pH 2–2.5 are $A_0(^{51}V) = 104 \times 10^{-4}$ cm^{-1} and $g_0 = 1.965$. An analogous trend is observed in the low temperature spectrum; $A_{\parallel}(^{51}V)$ is the same as that of the aqua ion (180×10^{-4} cm^{-1}) while $g_{\parallel}$ is slightly but significantly less (1.932 to be compared with the aqua ion value of 1.933).

The electronic spectra show a low-energy shift of the 770 nm absorption band, typical for the aqua ion, to 800 nm ($\varepsilon = 22$ M^{-1} cm^{-1}), while the higher energy shoulder (650 nm, $\varepsilon = 9$ M^{-1} cm^{-1}) is more pronounced than in the case of the aqua ion.

Potentiometric speciation results are presented in Table 1, where logβ values for the complexes are listed. Concentration distribution curves of the species formed at 2:1 ligand-to-metal molar ratio as a function of pH are presented in Figure 2. The speciation diagrams indicate that diphosphate forms two protonated species, $[VOAH_2]$ (minor) and $[VOAH]^-$, below pH 3. EPR spectroscopy is not able to distinguish the two species from each other and the measured parameters are also affected by the presence of residual aqua ion. Formation constant for the equilibrium $VO^{2+} + AH_2^{2-} \rightleftharpoons [VOAH_2]$ is $10^{2.23}$, which is in the range of the values of $10^{1.49}$ and $10^{3.20}$ reported so far for the stability constant of $[(VO)(H_2PO_4)]^+$.[17,18] This may suggest that AH_2^{2-} behaves as a monodentate ligand, coordinating through one end of the molecule, although weak chelation *via* the two slightly basic oxygens cannot be fully excluded. The analogous constant calculated for $[VOAH]^-$ is remarkably higher, $10^{6.75}$, which certainly indicates chelate formation.

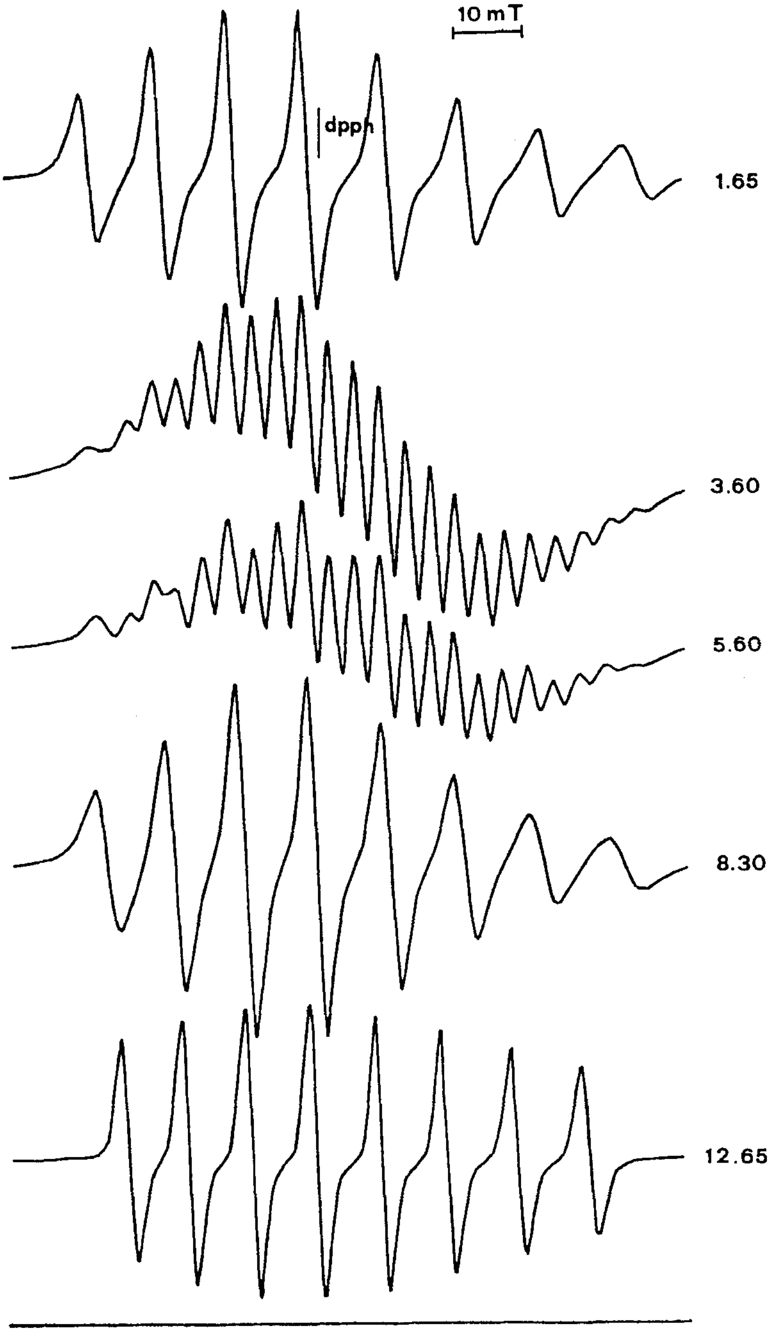


Figure 1 X-Band EPR spectra recorded at room temperature on aqueous solutions of VO^{2+} (0.1 M) and diphosphate at a ligand-to-metal molar ratio of 1:1 and varying pH.

Table 1 Protonation (log K), complex formation (log β) and equilibrium constants for the oxovanadium(IV) diphosphate and triphosphate systems at 25° C and I = 0.20 M (KCl).

	Diphosphate	Triphosphate
log K(HA)	8.25(3)	7.78(2)
log K(H_2A)	5.88(3)	5.36(3)
log K(H_3A)	1.66(12)	1.71(11)
$VOAH_2$	16.36(11)	15.17(15)
VOAH	15.00(5)	14.16(2)
VOA		10.33(2)
$VOAH_{-1}$	4.45(4)	2.72(3)
$VOAH_{-2}$		-6.06(5)
VOA_2H	23.18(8)	20.88(5)
VOA_2	17.67(5)	14.40(3)
$(VO)_3A_3$	42.55(7)	
$VO^{2+} + H_2A = VOAH_2$	2.23	2.03
$VO^{2+} + HA = VOAH$	6.75	6.38
$VO^{2+} + H_2A = VOAH + H^+$	0.87	1.02
$VO^{2+} + 2H_2A = VOA_2 + 4H^+$	-10.59	-11.84
$VOA_2H = VOA_2 + H^+$	-5.51	-6.48
Fitting[a] (cm^3)	1.08×10^{-2}	1.33×10^{-2}
No. of points	279	472

[a] Average difference between experimental and calculated titration curves expressed in cm^3 of titrant.

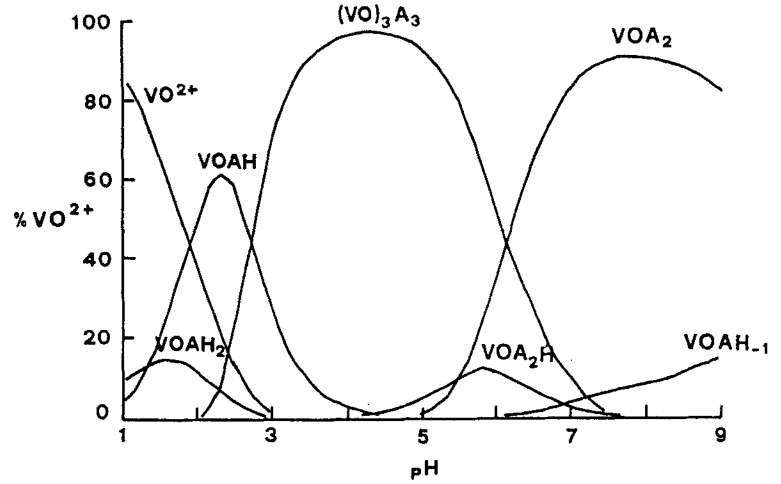


Figure 2 Speciation curves for complexes formed in the VO(IV)-diphosphate system, $c_{VO^{2+}} = 0.002$ M and $c_{ligand} = 0.004$ M. Charges are omitted for simplicity.

Above pH 3, *e.g.*, pH 3.6 and 5.6 in Figure 1, the isotropic EPR spectra consist predominantly of twenty-two equally spaced hyperfine lines with intensity ratios very close to the expected ones (1:3:6:10:15:21:28:36:42:46:48:48:46:42:. . .) for the interaction of one unpaired electron with three equivalent vanadium nuclei. This spectrum has already been reported and assigned to a cyclic trinuclear complex $[(VO)_3A_3]^{6-}$, this being the only structure which can account for the equivalence of the VO(IV) ions.[6–8] The magnetic parameters are $g_o = 1.965$ and $A_o(^{51}V) = 34 \times 10^{-4}$ cm^{-1} and the hyperfine coupling constant is about one third of that expected for a monomeric species with the same donor set around the metal ion. The EPR spectrum recorded at low temperature displays a broad resonance with no resolved hyperfine structure but the half-field $\Delta_{M_S} = 2$ band supports the trimetallic species. Failure to detect hyperfine patterns is probably due to the great number of EPR transitions expected for three exchange coupled oxovanadium(IV) ions, further complicated by zero field splitting effects operating in frozen solutions. Accordingly, a broad band, with only partial hyperfine splitting, characterizes the anisotropic spectra of the few cases of trimetallic VO(IV) systems reported so far.[19]

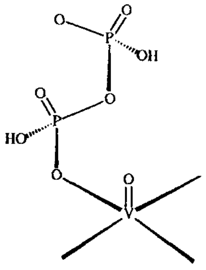
In the same pH range, pH-metry indicates the presence of a species $(VOA)_n$, with 1:1 ratio. The results of various speciation models of the system, reported in Table 2, substantiate that titration data could be fitted significantly better with the assumption of oligomeric species rather than a mononuclear VOA complex. However, titration points could be almost equally well fitted by dinuclear, trinuclear or tetranuclear species. If both mononuclear and oligonuclear species were included in the model the monomeric one was always rejected. The simultaneous assumption of more than one oligonuclear species generally resulted in the preferential formation of one of the oligonuclear species, but not always the same complex. The EPR features of this species, however, unambiguously prove that it is trinuclear with the binding mode depicted in Scheme 1.

Above pH 8 the trimetallic system is not observed and a new mono-metallic species is detected from the eight line isotropic EPR spectrum, $g_o = 1.967$ and $A_o(^{51}V) = 99 \times 10^{-4}$ cm^{-1}. These features are identical with those obtained in the case of excess ligand (see later); thus they are safely assigned to $[VOA_2]^{6-}$. However, the noticeable decrease of intensity of the EPR signal substantiates the predominance of polynuclear hydrolytic species. In very basic solution the system yields the EPR-active complex $[VO(OH)_3]^-$. The complete release of diphosphate from the metal coordination sphere is also reflected in the linewidth that is narrower than for the other complexes for which unresolved ^{31}P hyperfine coupling gives a contribution. Spectra of frozen solutions (even at metal concentrations as low as 0.002–0.004 M) parallel the complexation scheme outlined at room temperature. Concerning the detection of complex $[VOA_2]^{6-}$ at 1:1 ratio, it must be noted that in equimolar systems, only the pH range 2–6 was involved in evaluation of stability

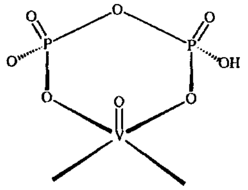
Table 2 Model selection studies in the oxovanadium(IV) diphosphate system.

Complex	Model 1	Model 2	Model 3	Model 4	Model 5
$VOAH_2$	16.98(11)	16.47(13)	16.26(18)	16.36(11)	16.02(30)
VOAH	14.80(4)	14.92(4)	14.99(4)	15.00(5)	15.05(4)
VOA	12.48(5)				
$VOAH_{-1}$	3.82(13)	4.33(4)	4.44(4)	4.45(4)	4.51(4)
VOA_2H	23.31(28)	23.19(10)	23.17(8)	23.18(8)	23.17(8)
VOA_2	18.18(9)	17.78(5)	17.68(5)	17.67(5)	17.62(5)
$(VO)_2A_2$		27.37(6)	26.54(23)		
$(VO)_3A_3$			42.47(12)	42.55(9)	
$(VO)_4A_4$					57.81(14)
Fitting[a] (cm^3)	1.86×10^{-2}	1.17×10^{-2}	1.08×10^{-2}	1.08×10^{-2}	1.14×10^{-2}
No. of points	279	279	279	279	279

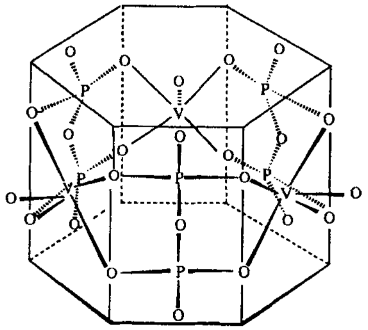
[a] Average difference between experimental and calculated titration curves expressed in cm^3 of titrant.



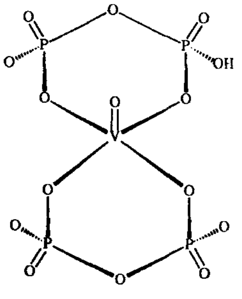
$VOAH_2$



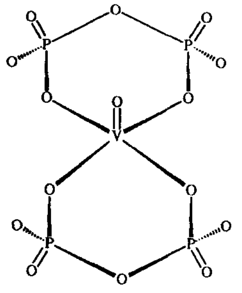
VOAH



$(VO)_3A_3$



VOA_2H



VOA_2

data because of rather long equilibration times, most likely due to slow oligomerization-olation reactions, in more basic solution. Therefore potentiometric data cannot be used to calculate speciation above pH 6 at 1:1 ratio. According to spectroscopic data, binary hydroxo complex formation occurs whereas the rest of VO(IV) can form bis-complexes, as was observed earlier.[6]

As the ligand-to-metal ratio is increased, mononuclear 2:1 complexes prevail over the trimetallic 1:1 species. Figure 3 shows EPR spectra of a frozen solution with $[VO^{2+}] = 0.004$ M and a ligand-to-metal ion ratio of 100. Increasing pH above 3 produces a continuous decrease of the ^{51}V parallel splitting, which is due only to the monometallic species without significant interference from the featureless signal of the residual trimetallic system. In the pH range 6–11, the value of the ^{51}V parallel coupling constant no longer changes, indicating that the formation of the bis-chelated complex $[VOA_2]^{6-}$ is complete; $g_{\parallel} = 1.937$ and $A_{\parallel}(^{51}V) = 176 \times 10^{-4}$ cm^{-1}. The corresponding electronic spectrum displays three optical bands at 400, 615 and 805 nm ($\varepsilon = 3$, 8 and 20 M^{-1} cm^{-1}, respectively). These values compare well with those of the trimetallic species, 400, 620 and 810 nm ($\varepsilon = 3$, 6 and 16 M^{-1} cm^{-1}, respectively), which is not surprising since the ligand environment around the VO^{2+} ion is the same in both complexes. $[VOA_2]^{6-}$ is a bis-chelated species, in fact the pK_a for the last dissociable proton, $pK_a(VOA_2H) = 5.52$, is more than two orders of magnitude lower than the value for the free ligand (8.25).

Calculated speciation curves indicate that, at ligand-to-metal ion ratios as high as 100, the dominant species (*ca* 90%) around pH 4.7 is $[VOA_2H]^{5-}$ in which one of the two ligands retains one proton. On this basis it is possible to assign the EPR

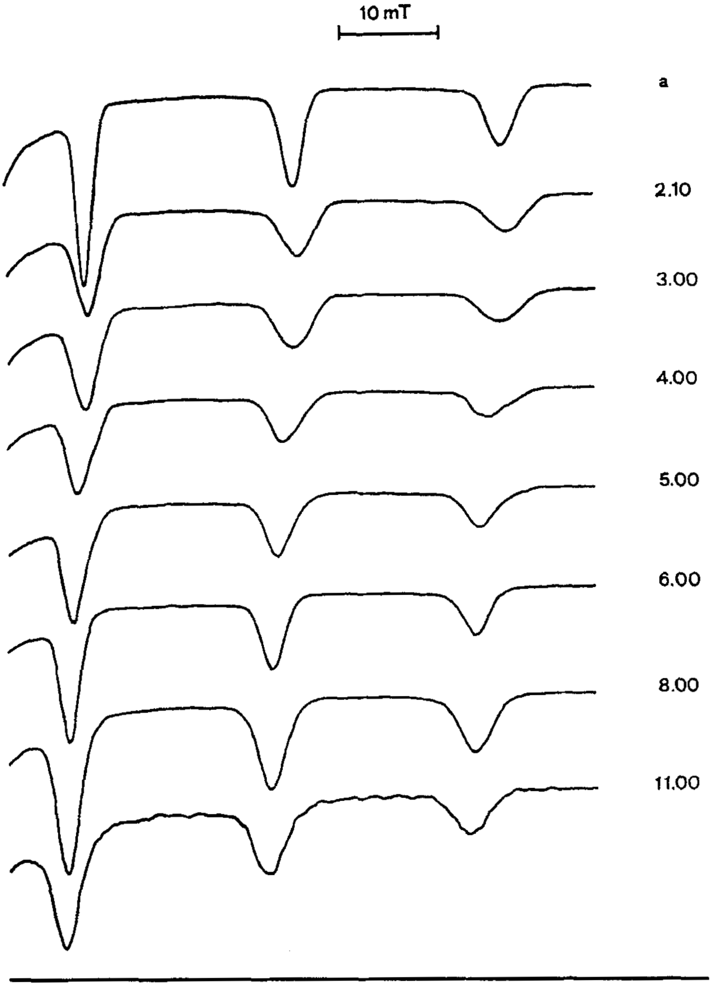


Figure 3 High-field parallel region of the EPR spectra recorded at 140 K on aqueous solutions of VO^{2+} (0.004 M) and diphosphate at a ligand-to-metal molar ratio of 100:1 and varying pH. Spectrum *a* is that of $[VO(H_2O)_5]^{2+}$.

parameters $g_{\parallel} = 1.934$ and $A_{\parallel}(^{51}V) = 177 \times 10^{-4}$ cm^{-1} and *d-d* absorptions 620 and 815 nm (ε = 13 and 23 M^{-1} cm^{-1}, respectively), all of which have been measured at the maximum extent of $[VOA_2H]^{5-}$ formation. Comparison with the corresponding species formed by triphosphate (see below) suggests that, similarly to the fully deprotonated complex $[VOA_2]^{6-}$, $[VOA_2H]^{5-}$ is also bis-chelated.

Triphosphoric acid exists as $H_3P_3O_{10}{}^{2-}$ above pH 1; this anion bears three dissociable protons with pK_a values 1.71, 5.36 and 7.78 respectively. These data compare fairly well with those already reported, *e.g.*, by Cini *et al.* (1.87, 5.46 and 7.81).[9] The difference between the two sets of data can be explained by the ionic strength dependence of the acidity.

In this case, the sequence of isotropic EPR spectra of an aqueous solution, even in the presence of a large excess of metal ion, does not detect polynuclear species such as the trimetallic complex formed by diphosphate. The reason probably lies in electrostatic and/or steric effects which hinder polynuclear assembly made up of three, negatively charged, mononuclear, 1:1 units.

EPR spectra of a frozen solution with $[VO^{2+}] = 0.004$ M and 2:1 ligand-to-metal ion ratio are presented in Figure 4. Even at $pH < 2$ the vanadyl ion appears to be coordinated by protonated forms of the ligand. Variation of parameters in the first step of complexation, increase of $A_{\parallel}(^{51}V)$ and, particularly, decrease of $g_{\parallel}$, is more pronounced than it is in the diphosphate-VO^{2+} system. The values

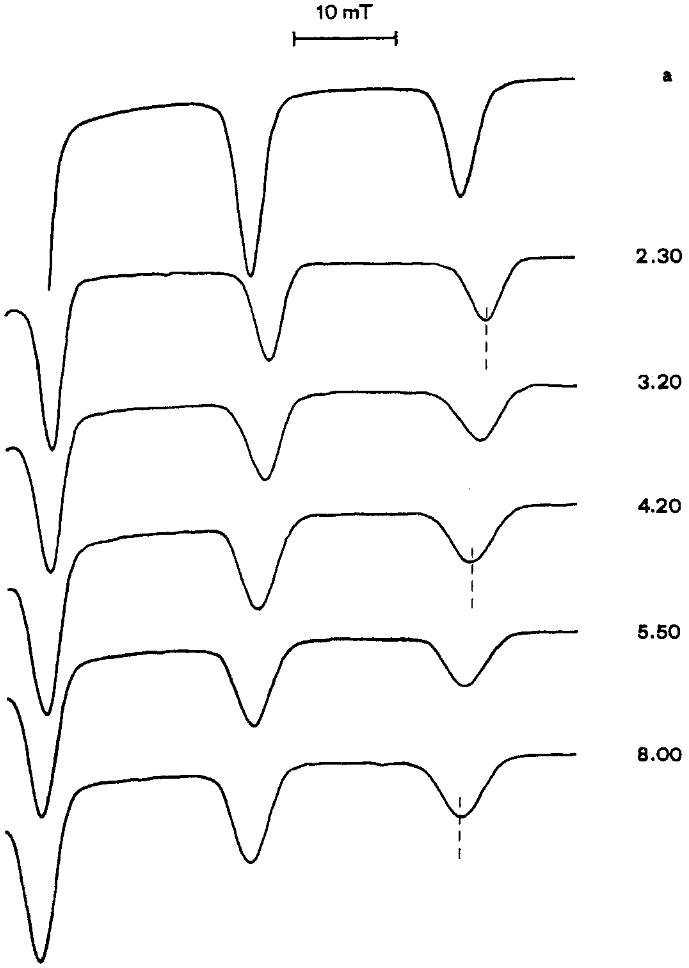
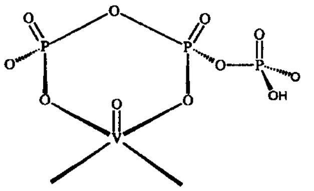


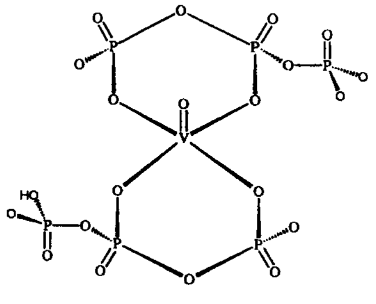
Figure 4 High-field parallel region of the EPR spectra recorded at 140 K on aqueous solutions of VO^{2+} (0.004 M) and triphosphate at a ligand-to-metal molar ratio of 2:1 and varying pH. Spectrum *a* is that of $[VO(H_2O)_5]^{2+}$.

$A_{\parallel}(^{51}V) = 182 \times 10^{-4}$ cm^{-1} and $g_{\parallel} = 1.929$ are measured around pH 2.5 and, as inferred from potentiometric data (Figure 5), they have a predominant contribution from the species $[VOAH]^{2-}$. Notably, the decrease of $g_{\parallel}$ and the increase of $A_{\parallel}$, as compared to the aqua ion, are rather unusual for VO(IV) complexes in solution and may be assumed as indicating 1:1 mono-chelated species (even in the case of ADP and ATP[20]). The constant for the equilibrium $VO^{2+} + AH^{4-} \rightleftharpoons [VOAH]^{2-}$ is $10^{6.38}$ which is only slightly lower than that measured for the same species formed by diphosphate; this shows that VOAH is a chelated complex (Scheme 2). Upon formation of the other major 1:1 complex $[VOA]^{3-}$, which however is never a single species, the EPR trend is reversed, *e.g.*, $g_{\parallel}$ increases and $A_{\parallel}$ decreases. The pK_a value for the last deprotonation of the coordinated ligand concomitant to the formation of $[VOA]^{3-}$ is 3.83, four orders of magnitude lower than that for the free ligand (7.78), a fact which suggests that the ligand acts as terdentate and forms two six-membered chelate rings.

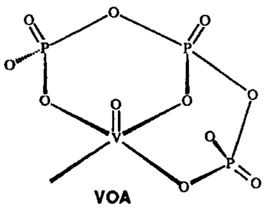
The monometallic complexes with a 2:1 stoichiometry are better characterized when higher ligand-to-metal ion ratios are considered. Distribution curves calculated for an aqueous solution with $[VO^{2+}] = 0.004$ M and 100:1 ligand-to-metal ion ratio show that, between pH 4 and pH 6, the prevailing complex is $[VOA_2H]^{7-}$, then $[VOA_2]^{8-}$ which, however, can not prevent hydrolysis above pH 9. These data allow us to assign to $[VOA_2H]^{7-}$ and $[VOA_2]^{8-}$ the following magnetic parameters measured on frozen solution EPR spectra: $[VOA_2H]^{7-}$, $g_{\parallel} = 1.935$ and $A_{\parallel}(^{51}V) = 178 \times 10^{-4}$ cm^{-1}; $[VOA_2]^{8-}$, $g_{\parallel} = 1.937$ and $A_{\parallel}(^{51}V) = 176 \times 10^{-4}$ cm^{-1}.



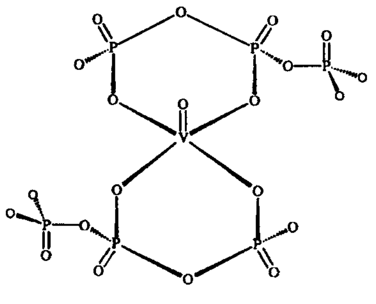
VOAH



VOA$_2$H



VOA



VOA$_2$

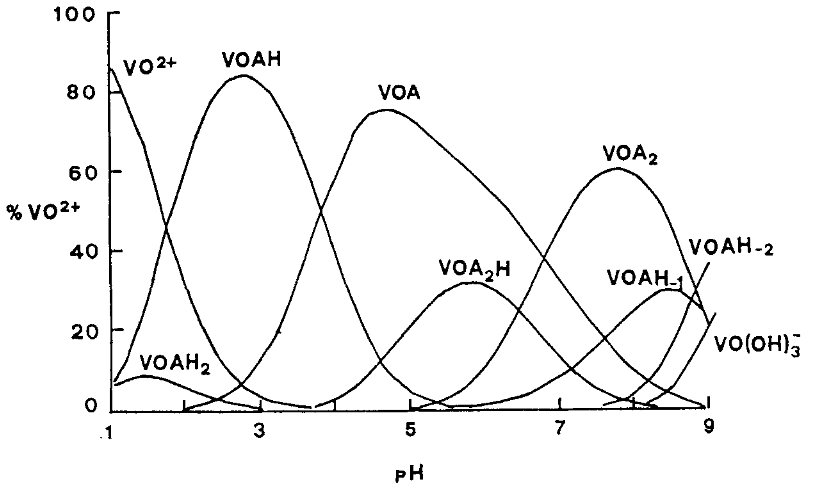


Figure 5 Speciation curves for complexes formed in the VO(IV)-triphosphate system, $c_{VO^{2+}} = 0.002$ M and $c_{ligand} = 0.004$ M.

Both species are chelated, a conclusion which can be drawn from thermodynamic considerations. As to $[VOA_2H]^{7-}$, the equilibrium constant for the reaction $[VOA]^{3-} + AH^{4-} \rightleftharpoons [VOA_2H]^{7-}$ is $10^{2.77}$, greater by about one order of magnitude than that for the bis-complex $[VO(H_2PO_4)_2]$,[18] notwithstanding unfavourable electrostatic effects. $\log K_2$ for $[VOA_2]^{8-}$ is 4.07; this value is the same as those measured for the corresponding complexes formed by ADP (4.12) and ATP (3.93)[20] for which the chelated arrangement of the polyphosphate moiety around the metal ion is inferred from spectroscopic evidence. As the value of $\log\beta_{(VOA_2)} - 2\log\beta_{(H_2A)}$ indicates, the triphosphate $[VOA_2]^{8-}$ complex is less stable than the diphosphate analogue, probably due to repulsive electrostatic effects which hinder the coordination of negatively charged ligands to 1:1 complexes which already possess negative charges. Owing to a greater negative charge in the complex, $pK_a(VOA_2H)$ for triphosphate is larger than that for diphosphate while reverse behaviour is observed for unbound ligands.

Electronic spectra are similar to, but not the same as, those of the diphosphate-VO^{2+} system. $[VOAH]^{2-}$ and $[VOA]^{3-}$ both contribute to the absorption band at 820 nm and the shoulder at 660 nm ($\varepsilon = 21$ and 10 M^{-1} cm^{-1}, respectively). $[VOA_2H]^{7-}$ is characterized by a maximum at 830 nm ($\varepsilon = 21$ M^{-1} cm^{-1}) and a better delineated shoulder at 660 nm ($\varepsilon = 8$ M^{-1} cm^{-1}, respectively).

On the whole, the results of this study confirm the need of the joint application of solution equilibrium and spectroscopic methods for a complete and unambiguous description of metal complex formation processes. In particular, in these systems, due to the involvement of only oxygen donors, extracting structural information on the sole basis of spectroscopic data is a rather difficult task. Nevertheless, distinctive trends may be found. The EPR parameters of the complexed species show only subtle differences as compared to those of aqua ion; however, the involvement of the first diphosphate chain in metal coordination seems to produce a decrease of $g_{\parallel}$ and an increase of $A_{\parallel}$, whereas the subsequent phosphate binding reverses this behaviour to a greater extent, the higher the degree of deprotonation of the coordinating groups. In all complexes the coordination of polyphosphate oxygens to VO(IV) produces a bathochromic shift of the low-energy absorption maximum typical of the aqua ion.

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References

1. D. Rehder, *Angew. Chem. Int. Ed. Engl.*, **30**, 148 (1991).
2. B.R. Nechay, L.B. Nanniga and P.S.E. Nechay, *Arch. Biochem. Biophys.*, **251**, 128 (1986).
3. G.M. Woltermann, R.A. Scott and G.P. Haight, Jr., *J. Am. Chem. Soc.*,**96**, 7569 (1974).
4. L.C. Cantley Jr., L. Josephson, R. Warner, M. Yanagisawa, C. Lechene and G. Guidotti, *J. Biol. Chem.*, **252**, 7421 (1977).
5. M.R. Hoffmann, R.A. Stern, P.H. Rieger and J.A. Edwards, *Inorg. Chim. Acta*, **19**, 181 (1976).
6. C.C. Parker, R.R. Reeder, L.B. Richards and P.H. Rieger, *J. Am. Chem. Soc.*, **92**, 5230 (1970).
7. A. Hasegawa, Y. Yamada and M. Miura, *Bull. Chem. Soc. Jpn.*, **42**, 846 (1969).
8. A. Hasegawa, *J. Chem. Phys.*, **55**, 3101 (1971).
9. R. Cini, G. Giorgi, F. Laschi, M. Sabat, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 575 (1969).
10. G. Gran, *Acta Chem. Scand.*, **4**, 559 (1950).
11. I. Nagypál and I. Fabián, *Inorg. Chim. Acta*, **61**, 109 (1982).
12. H.M. Irving, M.G. Miles and L.D. Pettit, *Anal. Chim. Acta*, **38**, 475 (1967).
13. L. Zékány and I. Nagypál, in 'Computational Methods for the Determination of Stability Constants', D. Legget, Ed., (Plenum Press, New York, 1985).
14. R. P. Henry, P.C.H. Mitchell and J.E. Prue, *J. Chem. Soc., Dalton Trans.*, 1156 (1973).
15. A. Komura, M. Hayashi and H. Imanaga, *Bull. Chem. Soc. Jpn.*, **59**, 2927 (1977).
16. A.E. Martell and R.M. Smith, in 'Critical Stability Constants', Vol. 6, (Plenum Press, New York, 1986).
17. A. A. Ivakin, Z.M. Voronova and L.D. Koorbatova, *Zh. Neorg. Khim.*, **20**, 1246 (1975).
18. W.C. Copenhafer, M.W. Kendig, T.P. Russell and P.H. Rieger, *Inorg. Chim. Acta*, **17**, 167 (1976).
19. T. Kiss, G. Micera, D. Sanna and H. Kozlowski, *J. Chem. Soc., Dalton Trans.*, 347 (1994).
20. E. Alberico, D. Dewaele, T. Kiss and G. Micera, *J. Chem. Soc., Dalton Trans.*, 425 (1995).