$Cr_2(CO)_8(C_5H_8N_2)_2$, 54067-84-4; $Mo_2(CO)_8(C_5H_8N_2)_2$, 55016-44-9; $W_2(CO)_8(C_5H_8N_2)_2$, 58602-27-0; $CrMo(CO)_8(C_5H_8N_2)_2$, 55016-43-8; $CrW(CO)_8(C_5H_8N_2)_2$, 58602-28-1; $MoW(CO)_8(C_5H_8N_2)_2$, 58602-29-2; $Cr_2(CO)_6(C_5H_8N_2)_3$, 30931-85-2; $Mo_2(CO)_6(C_5H_8N_2)_3$, 58602-30-5; $W_2(CO)_6(C_5H_8N_2)_3$, 58602-31-6; $Cr(CO)_4(C_7H_8)$, 12146-36-0; $Mo(CO)_4(C_7H_8)$, 12146-37-1; $W(CO)_4(C_7H_8)$, 12129-25-8; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_3(CH_3CN)_3$, 16800-47-8; $Fe_2(CO)_9$, 15321-51-4.

References and Notes

(1) A. J. Carty, *Organomet. Chem. Rev. A*, **7**, 191 (1972).
(2) M. Kilner, *Adv. Organomet. Chem.*, **10**, 115 (1972).
(3) S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, **57**, 389 (1973).
(4) D. Sellmann, *Angew. Chem. Int. Ed. Engl.*, **13**, 639 (1974), and references therein.
(5) R. W. F. Hardy, R. C. Burns, and G. W. Parshall, *Adv. Chem. Ser.*, **No. 100**, 219 (1971).
(6) G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **8**, 650 (1969).
(7) M. Kooti and J. F. Nixon, *J. Organomet. Chem.*, **76**, C29 (1974).
(8) R. J. Bennett, *Inorg. Chem.*, **9**, 2184 (1970).
(9) M. Herberhold and W. Golla, *J. Organomet. Chem.*, **26**, C27 (1971).
(10) M. Ackermann and L.-J. Kou, *J. Organomet. Chem.*, **86**, C7 (1975).
(11) M. Herberhold, W. Golla, and K. Leonhard, *Chem. Ber.*, **107**, 3209 (1974).
(12) P. G. Gassman and K. T. Mansfield, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., p 96.
(13) R. B. King, "Organometallic Syntheses", Vol. I, Academic Press, New York, N.Y., 1965.
(14) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).
(15) D. P. Tate, J. M. Augl, and W. R. Knipple, *Inorg. Chem.*, **1**, 433 (1962).
(16) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4422 (1974).
(17) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
(18) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
(19) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).
(20) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).
(21) M. Herberhold, K. Leonhard, and C. G. Kreiter, *Chem. Ber.*, **107**, 3222 (1974).

Contribution from the Department of Chemistry, University of California, Riverside, California 92502

Vanadium(IV) Gluconate Complexes

RENÉ GOOD and DONALD T. SAWYER*

Received September 26, 1975 AIC50714C

The complexes formed by oxovanadium(IV) with gluconate have been studied by spectrophotometry, circular dichroism, and polarography between pH 5 and pH 14. The stoichiometry of the complexes varies from a vanadium-to-gluconate ratio of 1:1 at pH 6.0 to 1:2 above pH 12. Both species give well-defined polarographic oxidation waves. The apparent formation constant, K_1', of the 1:1 complex at pH 6.0 is 2.2×10^3 M^{-1}; K_2' for the 1:2 complex in 0.5 M NaOH is 1.8×10^5 M^{-2}. The apparent equilibrium constant between the 1:1 and 1:2 complexes is 6.7×10^3 M^{-2}. Polarographic data indicate that oxovanadium(V) forms a transient complex with gluconate at pH 6 but is not complexed at pH 14.

There is increasing evidence that vanadium has a significant biological role, although it has been established as an essential element for only a few organisms.[1] Vanadium ions also can be substituted for the metals of metalloenzymes without loss in enzymatic activity and thereby provide an ESR probe.[2] Recently, the complexes of oxovanadium(IV) and vanadium(V) with uridine have been proposed as transition state analogues for ribonuclease.[3] The successful coupling of ATP hydrolysis with the ($VO_2^+ + H_2O_2$) redox system[4] provides support for the proposition that electron-transfer reactions occur simultaneously with the ATP–ADP reaction and for the conclusion that vanadium chemistry has substantial relevance to biology.

Gluconic acid (the carboxylic acid derivative of D-glucose) retains the polyhydroxy character of saccharides but is stable to oxidation. Most multicharged metal ions form stable complexes with gluconate ion, especially in alkaline media. A number of these have been studied in terms of electrochemistry, solution equilibria, and reaction stoichiometries.[5] Use of proton NMR has provided insight to the most likely ligand coordination sites.[6] For lead(II) and bismuth(III) the carboxylate oxygen and the α-, β-, and γ-hydroxy oxygens of gluconate are bonded to the metal under basic conditions.

Although several ligands that contain one hydroxyl group and a carboxylate group form complexes with oxovanadium(IV),[7] data for alkaline conditions are limited. Because the formation of stable complexes by saccharides with oxovanadium(IV) in basic media has been known for a long time, similar behavior is to be expected of gluconate ion.

The present study has been undertaken to characterize the electrochemistry and solution equilibria of the complexes of oxovanadium(IV) and oxovanadium(V) with gluconate ion over a wide range of pH values. It results from a continuing interest in model complexes that mimic the chemistry of biological transition metals that are involved in oxidation–reduction reactions.

Experimental Section

Equipment. Spectrophotometric data were obtained with a Cary Model 14 recording spectrophotometer. The circular dichroism measurements were made with a Jasco Model ORD/CD/UV-5 optical rotatory dispersion spectrometer. Polarographic data were recorded with a Sargent Model XV recording polarograph at 25 ± 0.1 °C. The diffusion currents were determined for maximum current (envelope of the tops of the oscillations) and were corrected for residual current. Potentials were measured and reported vs. the saturated calomel electrode (SCE). For the dropping-mercury electrode, the rate of flow of mercury was 2.32 mg/s and the drop time was 3.50 s (without an applied potential). pH measurements were made either with a Corning Model 12 pH meter or a Leeds and Northrup pH meter; the meters were standardized with NBS buffers. Magnetic susceptibility determinations were made by NMR[9] with diamagnetic corrections through use of Pascal's constants.[10] NMR spectra were recorded on a Varian A-60D spectrometer.

Reagents. The vanadium(IV) solutions were prepared from vanadyl sulfate, $VOSO_4 \cdot 1.5H_2O$ (Fisher Scientific Co.) which was found to be 99.4% pure on the basis of permanganate titrations. Vanadium(V) solutions were made from purified NH_4VO_3 (Fisher Scientific Co.); $NaVO_3 \cdot nH_2O$ also was used for some qualitative experiments. Sodium gluconate solutions were prepared determinately from D-gluconodelta-lactone (Matheson Coleman and Bell). The purity of the lactone was determined by back-titrating with standard acid a solution to which excess standard base had been added. The lactone was found to be 99.7% pure and to have a melting point of 152–153 °C.

Above pH 4, solutions that contain oxovanadium(IV) are highly sensitive to air oxidation. To prevent this, the reagent solutions were degassed with and protected by an argon atmosphere. During the preparation of a solution to be examined, argon was bubbled through the initial and resulting solutions. Uv cells were stoppered tightly

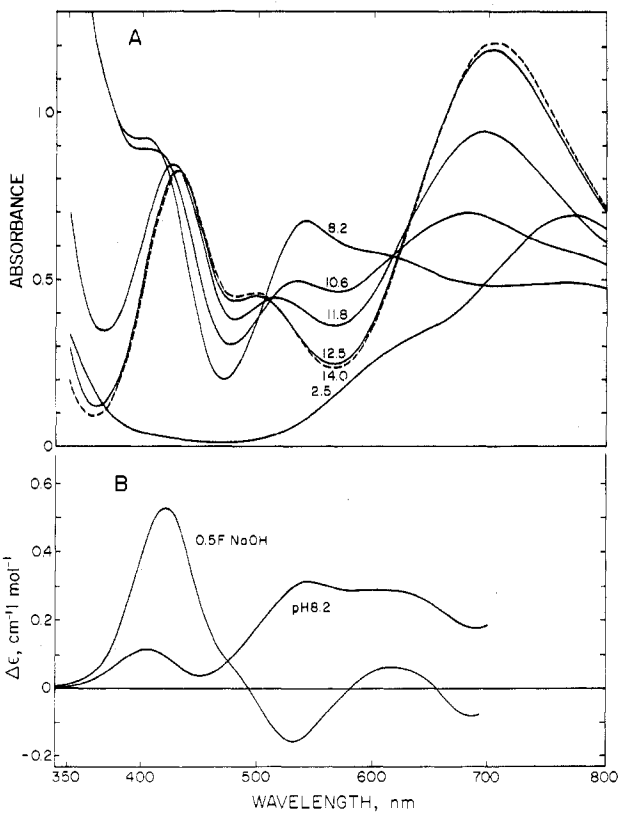

Figure 1. (A) Absorption spectra of the complexes formed by oxovanadium(IV) and gluconate ion as a function of pH. Solution conditions: 0.040 M $VOSO_4$, 0.120 M GH_4^-, pH values indicated. Cell path length is 1 cm. (B) CD spectra for the same solution conditions as A.

and no change was observed in the spectra within a few hours. pH titrations were performed under argon in a Leeds and Northrup electrochemical cell.

Results

Complexation by gluconate ion of oxovanadium(IV) and, to some extent, of oxovanadium(V) is observed in the pH range from pH 5 to pH 14. The present study has been limited to this range because oxidation of gluconic acid by vanadium(V) is likely in acidic media[11] and the interaction between gluconate and oxovanadium(IV) is weak or nonexistent in acidic solutions on the basis of spectroscopic evidence.

Spectroscopy. Solutions of vanadyl sulfate owe their blue color to the $V^{IV}O(H_2O)_5^{2+}$ entity.[12] In acidic medium, the addition of gluconate does not noticeably modify this color. However, addition of sodium hydroxide causes the solution to turn violet at pH 5; further addition of base results in a green solution above pH 12. Both the violet and green colors are more intense than the initial blue. In the absence of gluconate, the addition of base to vanadyl solutions causes either the precipitation of the yellow $VO(OH)_2$ species[13] or the appearance of a brown color, which probably is due to $VO(OH)_3^-$.[14]

Figure 1A illustrates the absorption spectra for vanadium(IV) in the presence of excess gluconate ion from pH 2.5 to pH 14. Three main absorption bands are observed with the maximum at 540 nm corresponding to the violet solution and those at 430 and 704 nm corresponding to the green solution.

Two isosbestic points (at 507 and 620 nm) are observed for the set of spectra in Figure 1A. These result from the equilibrium between two species, a complex that is predominant at pH values close to neutrality and a complex that is stabilized in strongly basic solutions. The latter has two main chromophores at 704 and 430 nm and the neutral species

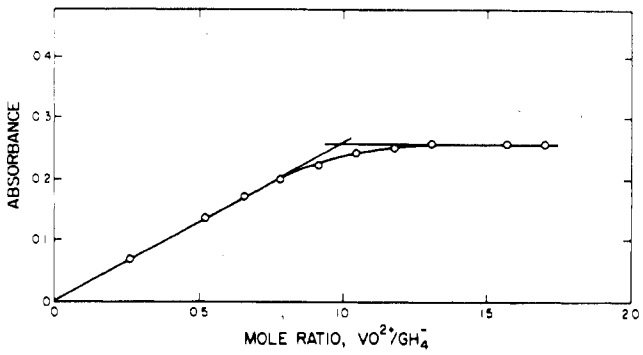

Figure 2. Mole ratio study at 540 nm for the oxovanadium(IV)-gluconate complex at pH 6.0 for a 0.040 M GH_4^- solution. Absorbance values have been baseline corrected.

a single major chromophore at 540 nm. This explains the occurrence of two isosbestic points for a two-species equilibrium. There is a possible third isosbestic point at 425 nm which could arise from interaction with the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ bands of gluconate. These bands are known to undergo a bathochromic shift as a consequence of complexation.[6] However, this does not alter the conclusion that the spectra result from an equilibrium between two oxovanadium(IV) gluconate complexes.

The stoichiometries of these two vanadyl complexes have been established by mole ratio studies. Figure 2 indicates that a 1:1 complex is formed at pH 6.0 between oxovanadium(IV) and gluconate ion. Although this type of study does not allow definite conclusions as to the absence of a 1:2 metal–ligand complex, the polarographic data support such a conclusion. The apparent stability constant, K_1', for the 1:1 complex ($V^{IV} + L \rightleftarrows V^{IV}L$) is estimated to be 2.2×10^3 M^{-1} on the basis of the difference between the extrapolated and actual absorbances at a mole ratio of 1 in Figure 2; L represents the anion of D-gluconic acid.

A mole ratio experiment similar to that of Figure 2, but at 704 nm with variable gluconate concentrations and a constant vanadyl concentration in 0.5 M NaOH, indicates that the green complex has a 1:2 vanadyl-to-gluconate stoichiometry. The apparent stability constant, K_2', for this complex ($V^{IV} + 2L \rightleftarrows V^{IV}L_2$) is estimated to be 1.8×10^5 M^{-2}. A plot of the absorbance at 704 nm vs. pH for 0.04 M vanadyl ion in the presence of excess gluconate ion (0.12 M) yields a curve with a well-defined break whose midpoint is at pH 11.4. Hence, the apparent equilibrium constant between the 1:1 and 1:2 complexes ($V^{IV}L + L + OH^- \rightleftarrows V^{IV}L_2$) is 6.7×10^3 M^{-2}.

To characterize further the solution equilibria of the oxovanadium(IV) gluconate complexes, a 1:6 mole ratio of vanadyl ion and gluconate ion has been titrated with NaOH (actually, an excess of base has been back-titrated with acid to avoid the slow lactone–gluconate equilibria that occur at low pH values). The result is a well-defined end point at pH 7.2 for 2 equiv of base per vanadyl ion and an inflection at pH 10.5 for 3 equiv of base per vanadyl ion.

As expected, acidic and basic solutions of gluconate ion and of vanadyl sulfate do not exhibit circular dichroism (CD) bands at wavelengths longer than 300 nm. However, when vanadyl ion and gluconate ion are combined, a stereospecific reaction takes place to give one or more optically active complexes. As illustrated by Figure 1B, the CD spectrum for near-neutral conditions is significantly different from that observed for strongly basic conditions. Five bands are observed for the CD spectrum recorded in 0.5 M NaOH; at pH 8.2 only four appear to be present. The signs of the maxima do not change, except for the band at 530–540 nm, which does not shift as much in the CD spectrum as it does for the absorption spectrum.

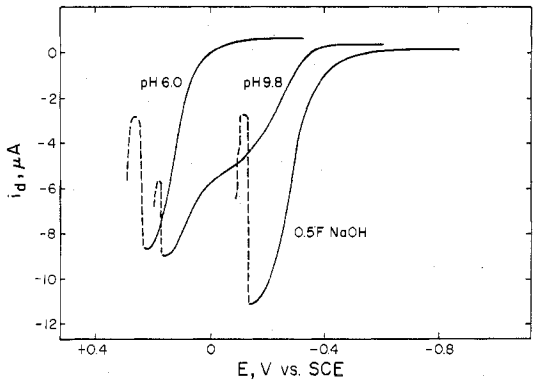

Figure 3. Polarographic oxidation waves for 5 mM $VOSO_4$ in 0.5 M GH_4^- solutions at various pH values. The dotted lines represent a surface reaction and the beginning of the mercury oxidation wave. In the absence of vanadyl ion, mercury dissolution occurs at −0.1 V for the 0.5 M NaOH solution, +0.2 V for the pH 9.8 solution, and +0.3 V for the pH 6.0 solution.

Table I. Polarographic Parameters for the Two Oxovanadium(IV) Gluconate Complexes[a]

	Electrode reaction	$E_{1/2}$, V vs. SCE	I_{max}	$E_{3/4} - E_{1/4}$, V
pH 6.0	$V^{IV} \rightarrow V^{V}$	0.118	0.79	0.065
0.5 M NaOH	$V^{IV} \rightarrow V^{V}$	−0.280	0.985	0.080

[a] Solution conditions: 0.005 M VO^{2+} and 0.5 M gluconate; temperature 25.0 ± 0.1 °C.

Electrochemistry. Neutral solutions of oxovanadium(IV) in the presence of 0.5 M gluconate ion exhibit well-defined polarographic oxidation waves as illustrated by Figure 3. Part of the diffusion current plateau is obliterated by a surface reaction and the oxidation wave of mercury. With increasing pH a second oxidation wave appears, with a proportionate decrease in the height of the first wave. This second wave is less reversible than the first wave; the general features of the polarographic waves are summarized in Table I. On the basis of the spectrophotometric evidence the first wave apparently corresponds to the oxidation of the 1:1 vanadyl gluconate complex, and the second wave, to the oxidation of the 1:2 complex.

The polarographic data are in accord with the conclusion that the equilibrium between the two vanadyl complexes is shifted completely to the 1:1 complex at pH 6.0. If this was not the case, a second oxidation wave should be observed (assuming the equilibrium between them is slow). In the case of the 1:2 complex in 0.5 M NaOH, the presence of a wave with a half-wave potential more positive than that of the principal wave cannot be determined. Therefore, the dependence of the diffusion current for the latter wave on oxovanadium(IV) concentration has been determined; i_d varies linearly with the concentration from 2.5×10^{-4} to 2.5×10^{-2} M vanadyl ion and follows the relation

$$i_d = I_{max} C m^{2/3} t^{1/6} \quad (1)$$

where i_d is in μA and C in mmol/l. The diffusion current constant, I_{max}, for these conditions is listed in Table I. The zero intercept and the straight-line dependence of this anodic wave implies that it represents all of the vanadium(IV) in solution and that the 1:1 form of the complex is essentially absent in 0.5 M NaOH solutions.

Although neither of the polarographic waves of Figure 3 (and Table I) meets the criteria for thermodynamic reversibility ($E_{3/4} - E_{1/4} = 0.056$ V), their deviation is small enough to encourage some quantitative interpretations of the nature of the complex species in solution and their oxidation reactions. As expected, the half-wave potential of both anodic waves is independent of the vanadyl concentrations. The effect of varying the gluconate ion concentration upon the half-wave potentials of the two anodic waves is illustrated by Figure 4. For reversible reactions the slopes of the curves obey the relation[15]

$$\frac{d(E_{1/2})_c}{d(\log C)} = \frac{-0.059p}{n} \quad (2)$$

where n is the number of electrons in the anodic reaction and p the number of ligands per metal ion that are gained in the oxidation step.

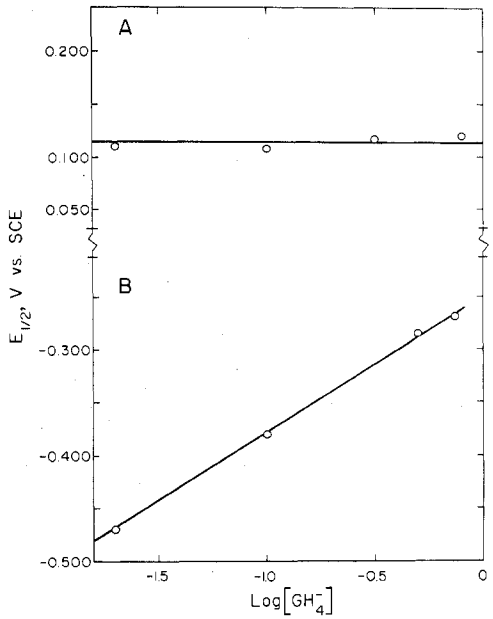

Figure 4. Plot of $E_{1/2}$ vs. log [GH_4^-] at pH 6.0 (curve A) and in 0.5 M NaOH (curve B) for the polarographic oxidation of 5 mM VO^{2+} ion in the presence of gluconate.

For the wave at pH 6.0, Figure 4A indicates that there is no change in the number of gluconate ions per vanadium during the oxidation of the complex from vanadium(IV) to -(V). The spectrophotometric data for the vanadium(IV) complex indicate a 1:1 metal:ligand stoichiometry at this pH. Hence, vanadium(V) must form a 1:1 complex, at least upon initial electrochemical formation. Polarographic studies of NH_4VO_3 solutions at pH 6.0 in the presence of gluconate did not give useful results because the reduction wave is obscured by the mercury dissolution reaction of the dropping-mercury electrode.

The slope of the curve of Figure 4B yields a value of −2.17 for p in eq 2. This result indicates that vanadium(V) is not complexed by gluconate ion in strongly basic media. Polarographic studies of NH_4VO_3 in strongly basic gluconate solutions did not prove useful.

Both the hydroxyl and gluconate ions can act as ligands in the system. Hence, the effect of pH on the half-wave potential of the oxovanadium(IV) complexes has been determined. In its short range of existence as a main species, i.e., pH 5–8.5, the 1:1 complex has a half-wave potential which is essentially independent of pH. The same is true for the half-wave potential due to the 1:2 complex, which is independent of base concentration from pH 11 to 1 M NaOH. In the region where both waves are present (pH 9–10.5) there is a shift to negative potentials as the pH is increased, which probably indicates that the intercomplex equilibrium is slow and that there is a gain in hydroxyl ions for the high-pH complex.

NMR. The proton NMR spectrum of a 1:1 solution of $NaVO_3$ and gluconate ion in D_2O at pD 6.0 is the same as that for gluconate ion alone. This indicates that the complex

Table II. Tentative Assignment of the Transitions Observed for the Two Complexes of Oxovanadium(IV) and Gluconate

pH	VO^{2+}:GH_4^- mole ratio	Absorption max λ, nm	Absorption max E, kK	Transition d-orbital representation	Transition MO representation
8.2	1:1	540	18.5	$d_{x^2-y^2} \leftarrow d_{xy}$	$b_1 \leftarrow b_2$
		400	25.0	$d_{z^2} \leftarrow d_{xy}$	$a_1 \leftarrow b_2$
14.0	1:2	704	14.2	$d_{xz}, d_{yz} \leftarrow d_{xy}$	$e_1 \leftarrow b_2$
		495	20.2	$d_{x^2-y^2} \leftarrow d_{xy}$	$b_1 \leftarrow b_2$
		430	23.3	$d_{z^2} \leftarrow d_{xy}$	$a_1 \leftarrow b_2$

of vanadium(V) initially formed during the polarographic experiment probably is unstable and is hydrolyzed in a subsequent step. Unfortunately, the NMR experiments require concentrations that are 100 times greater than those for the polarographic data.

A similar situation is found in 0.5 M NaOD for 1:1 solutions of $NaVO_3$ and gluconate ion; the CH proton resonance of gluconate is unaffected by the presence of $NaVO_3$. Thus, in strongly basic media, vanadium(V) generated by electrochemical oxidation of vanadyl ion and by dissolution of $NaVO_3$ shows the same behavior. This is probably due to the absence of polyvanadates which complicate the picture at lower pH values.

Discussion and Conclusions

Spectroscopy. The assignments of the bands in Figure 1A are not straightforward, and even for the most symmetrical oxovanadium complexes they have been the subject of considerable discussion.[7,16] However, on the basis of the Ballhausen and Gray[12] scheme, the assignments in Table II can be made. The band at 640 nm in Figure 1 for the pH 2.5 solution (previously assigned to the $b_1 \leftarrow b_2$ transition[12]) persists at pH 8.2. Moreover, the circular dichroism spectra in Figure 1B indicate that this band is present even at pH 14. This could indicate that the maximum at 540 nm represents the $a_1 \leftarrow b_2$ transition. In which case the 430-nm band would be due to a low-intensity spin-forbidden charge-transfer transition.

Although several circular dichroism studies of vanadyl complexes have been reported,[17,18] the molecular basis for the observed optical activity has not been determined. Likewise, for the oxovanadium(IV)–gluconate complexes (Figure 1B) the origin of the CD bands cannot be assigned. The optical activity may be transmitted from the chiral carbon atoms to the d orbital of the metal, or a chiral complex may be formed. The g factor[19] ($g = \Delta\epsilon_{CD}/\epsilon_{abs}$) for the well-defined CD maximum at 430 nm (Figure 1) has a value of 0.024. For a spin-allowed transition in an optically active molecule, this would indicate an allowed magnetic dipole transition with a low oscillator strength. The value of the g factor is dependent upon the intensity of other symmetry-allowed transitions.

Solution Equilibria. At pH 6.0, the apparent stability constant, $K_1' = 2.2 \times 10^3\ M^{-1}$, for the 1:1 complex corresponds to the overall formation equation

$$VO(OH)_2 + GH_4^- \rightleftarrows VO(OH)_2GH_4^- \quad K_1' \tag{3}$$

The ionic form of the vanadyl group is unknown in the absence of gluconate ion at pH 6; the $VO(OH)_2$ designation is arbitrary but consistent with the known behavior of the group at near-neutral conditions. The pK_a of a hydroxy group usually is lowered when an adjacent function forms a metal–ligand bond, which might prompt one to suggest a chelate reaction such as

$$VO(OH)_2 + GH_4^- \rightleftarrows VO(OH)GH_3^- + H_2O \tag{4}$$

with a gluconate as a dianion. This possibility must be regarded as unlikely at pH 6, because the second pK_a of gluconate is too high to be determined in water. However, weak chelation is thought to occur, in which nonionized alcohol groups replace coordinated water molecules.

Other metal–gluconate systems are known to have several metal–ligand stoichiometries at a given pH. This is particularly true for the spectroscopically related copper(II)–gluconate system,[20] where the 1:1 complex is converted to a 1:2 complex when the ratio of gluconate to copper exceeds 12. In the present case, even a ratio of 120 does not result in a 1:2 complex in detectable amounts.

In basic solutions vanadium(IV) has been shown to be present mainly as $VO(OH)_3^-$.[14] Hence, on the basis of the spectrophotometric and polarographic results, the formation reaction for the 1:2 complex in a 0.5 M NaOH solution is

$$VO(OH)_3^- + 2GH_4^- \rightleftarrows VO(OH)(GH_3)_2^{3-} + 2H_2O \quad K_2' \tag{5}$$

with $K_2' = 1.8 \times 10^5\ M^{-2}$. Also, the experimental results indicate that the pH-dependent equilibrium between the 1:1 and 1:2 complexes can be represented by

$$VO(OH)_2GH_4^- + OH^- + GH_4^- \rightleftarrows VO(OH)(GH_3)_2^{3-} + 2H_2O \quad K_{eq}' \tag{6}$$

with $K_{eq}' = 6.7 \times 10^3\ M^{-2}$. The latter has been evaluated from a plot of the absorbance for the 1:2 species vs. pH. As indicated by eq 6, the gluconate ligands in the 1:2 complex are assumed to be dianions. Such an assumption is well founded on the basis of the strong chelating properties of gluconate in strongly basic solutions. Furthermore, the mere addition of a ligand bound in a manner similar to the weak 1:1 complex could not account for the marked visible and CD spectral changes.

Hydroxide ion is a better ligand than either the deprotonated carboxylate or the hydroxyl functions of gluconate. However, the addition of large quantities of sodium hydroxide to a basic solution of the 1:2 complex does not modify its visible spectrum. This indicates a stabilization of the gluconate bonds through a chelate effect. The formation of the 1:2 complex can be envisioned as a stepwise process (eq 7–10), in which

$$VO(OH)_2GH_4^- \rightleftarrows VO(OH)GH_3^- + H_2O \tag{7}$$

$$VO(OH)GH_3^- + GH_4^- \rightleftarrows VO(OH)GH_3GH_4^{2-} \tag{8}$$

$$VO(OH)GH_3GH_4^{2-} + OH^- \rightleftarrows VO(OH)_2GH_3GH_4^{3-} \tag{9}$$

$$VO(OH)_2GH_3GH_4^{3-} \rightleftarrows VO(OH)(GH_3)_2^{3-} + H_2O \tag{10}$$

an OH^- group is eliminated as the chelate ring forms. The deprotonation of the hydroxy group of the gluconate ligand is believed to occur while the molecule is bound by the carboxylate group.

Structural Considerations. Under neutral conditions two coordination positions of the 1:1 oxovanadium(IV)–gluconate complex are occupied by OH^- groups, which leaves three other sites to be occupied by the ligand and water. While NMR data[6] indicate that the α-hydroxy group is involved in binding at high pH values, nothing is known concerning its participation in neutral solutions. In a similar way, the number of coordination sites filled by gluconate can only be guessed, but is felt to be at least 2.

In basic solutions, the data indicate that only one OH^- group is bound to the 1:2 oxovanadium(IV)–gluconate complex, with the remaining four coordination sites occupied by the two gluconate ligands to form two chelate rings via a deprotonated alcohol group. Previous NMR studies of gluconate complexes[6] indicate that the α-alcohol of gluconate is the most prone to form a chelate ring in conjunction with the carboxylate group. This is supported by two additional considerations: first, if the pK_a of an alcohol group is lowered by complexation of the carboxylate group, the α-alcohol should be the most affected;

second, coordination via this group forms a five-membered chelate ring, which is expected to bring about more stabilization than other modes of bidentate coordination. A structural model for the complex indicates that this ring structure can be achieved without strain.

Gluconate molecules are bulky and probably fit most easily in the equatorial plane, with the OH^- group in the axial position. This structure is encountered with the bis(acetylacetonato)oxovanadium(IV) complex;[21] the OH^- group can be replaced by Lewis bases, in particular amines.[22]

Oxovanadium(IV) forms 2:2 dimers with tartrate[23] in which spin pairing occurs between the two d electrons of vanadium. Magnetic susceptibility measurements of the 1:1 and 1:2 complexes of oxovanadium(IV) and gluconate yield values that essentially are identical with those obtained for a vanadyl sulfate solution. This indicates the absence of dimers with spin pairing but does not preclude the formation of non-spin-paired dimers.

Reactions at the Mercury Electrode and Vanadium(V) Complexes. In the intermediate situation where both the 1:1 and 1:2 oxovanadium(IV)–gluconate complexes are present, polarographic data indicate the uptake of hydroxyl ions during the oxidation reaction. However, the limited pH range for this condition makes quantitative conclusions impossible. However, for conditions where only one of the complexes is present, several quantitative conclusions are possible.

At pH 6, Figure 4A illustrates that the gluconate concentration does not affect the oxidation half-wave potential, which implies that the half-reaction can be expressed as

$$VO(OH)_2(GH_4)^- \rightarrow VO(OH)_2(GH_4) + e^- \quad (11)$$

There are numerous possibilities for the reactions which follow, mainly because of the presence of polyvanadates at this pH.

The absence of NMR evidence for complexation in a 1:1 solution of $NaVO_3$ and gluconate at pD 6.0 may be related to the polarographic data in two ways: first, the vanadium(V)–gluconate complex formed electrochemically may be unstable and only exist at the electrode surface for a brief period of time; second, due to sensitivity restrictions, NMR measurements have to be made in solutions whose metal concentration is 100 times higher than for polarography. Because the distribution of polyvanadates is dependent on concentration at pH values close to neutrality, the species in solution may differ from one method to the other.

In 0.5 M NaOH, the 1:2 oxovanadium(IV)–gluconate complex has an oxidation wave whose half-wave potential shifts with gluconate concentration, as shown in Figure 4B. Also, the proton NMR spectra are identical for a strongly basic solution of gluconate ion, whether $NaVO_3$ is added or not. This negative evidence is not conclusive by itself, but, in conjunction with the spectrophotometric and polarographic data, it establishes that vanadium(V) is not complexed by gluconate in strongly basic media. This result is in agreement with similar observations for the complexes of vanadium(V) and several polyaminocarboxylic acids.[24] Hence, on the basis of the slope of the curve in Figure 4B the oxidation reaction can be expressed as

$$VO(OH)(GH_3)_2^{3-} + H_2O \rightarrow VO(OH)_3 + 2GH_4^- + e^- \quad (12a)$$

with a post chemical reaction

$$VO(OH)_3 + 3OH^- \rightarrow VO_4^{3-} + 3H_2O \quad (12b)$$

The monomeric tetrahedral vanadate ion is a well-established species in strongly basic media.[25]

Acknowledgment. This work was supported by the National Science Foundation under Grant No. MPS73-05204. We also are grateful to the Stiftung für Stipendien auf dem Gebiete der Chemie, Basel, Switzerland, for a postdoctoral fellowship to R.G.

Registry No. VO^{2+}, 20644-97-7; GH_4^-, 608-59-3; $VO(OH)_2GH_4^-$, 58747-11-8; $VO(OH)(GH_3)_2^{3-}$, 58672-98-3.

References and Notes

(1) (a) T. G. F. Hudson, "Vanadium: Toxicology and Biological Significance", Elsevier, New York, N.Y., 1964; (b) J. H. Swinehart, W. R. Biggs, D. J. Halko, and N. C. Schroeder, *Biol. Bull. (Woods Hole, Mass.)*, **146**, 302 (1974); (c) D. B. Carlisle, *Proc. R. Soc. London, Ser. B*, **171**, 31 (1968).
(2) (a) J. J. Fitzgerald and N. D. Chasteen, *Biochemistry*, **13**, 4338 (1974); (b) R. J. DeKoch, D. J. West, J. C. Cannon, and N. D. Chasteen, *Biochemistry*, **13**, 4347 (1974).
(3) R. N. Lindquist, J. L. Lynn, Jr., and G. E. Lienhard, *J. Am. Chem. Soc.*, **95**, 8762 (1973).
(4) G. M. Woltermann, R. A. Scott, and G. P. Haight, Jr., *J. Am. Chem. Soc.*, **96**, 7569 (1974).
(5) D. T. Sawyer, *Chem. Rev.*, **64**, 633 (1964).
(6) D. T. Sawyer and J. R. Brannan, *Inorg. Chem.*, **5**, 65 (1966).
(7) (a) J. Selbin, *Chem. Rev.*, **65**, 153 (1965); (b) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966); (c) "Gmelins Handbuch der anorganischen Chemie", Vol. 48, 1968, p 533.
(8) V. K. Zolotukhin, *Zh. Prikl. Khim. (Leningrad)*, **10**, 1656 (1937).
(9) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(10) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry, Principles and Methods", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y., 1960, Chapter 6.
(11) Vinh-Chon-Thanh, M. Guernet, and M. Chaigneau, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 1311 (1971).
(12) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
(13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972, p 825.
(14) W. C. Copenhafer, M. Iannuzzi, C. P. Kubiak, and P. H. Rieger, Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1975, No. INOR 169.
(15) L. Meites, "Polarographic Techniques", Interscience, New York, N.Y., 1965, p 268.
(16) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.
(17) (a) K. M. Jones and E. Larsen, *Acta Chem. Scand.*, **19**, 1210 (1965); (b) H. P. Jensen and E. Larsen, *ibid.*, **25**, 1439 (1971).
(18) K. P. Callahan, Ph.D. Dissertation, University of Calif., Riverside, Calif., 1969.
(19) (a) W. Kuhn, *Trans. Faraday Soc.*, **26**, 293 (1930); (b) W. Kuhn, *Annu. Rev. Phys. Chem.*, **9**, 417 (1958).
(20) R. L. Pecsok and R. S. Juvet, Jr., *J. Am. Chem. Soc.*, **77**, 202 (1955).
(21) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).
(22) R. T. Claunch, T. W. Martin, and M. M. Jones, *J. Am. Chem. Soc.*, **83**, 1073 (1961).
(23) R. E. Tapscott, R. L. Belford, and I. C. Paul, *Coord. Chem. Rev.*, **4**, 323 (1969).
(24) L. W. Amos and D. T. Sawyer, *Inorg. Chem.*, **11**, 2692 (1972).
(25) M. T. Pope and B. W. Dale, *Q. Rev. Chem. Soc.*, **22**, 527 (1968).