into the position formerly occupied by the water to complete the octahedral coordination around the nickel.

Figure 3 represents the octahedral coordination around the nickel. The configuration of atoms can be thought of as two parallel equilateral triangles with the nickel ion between them. One triangle has the three coordinating nitrogens (N_1, N_2, N_3) at its vertices and has an average side of 2.75 ± 0.004 Å. The other triangle has the three coordinating oxygens (O_1, O_2, O_3) at its vertices with an average side of 2.90 ± 0.006 Å. The average distance between a nitrogen and the two nearest oxygens on the parallel triangle is 3.00 ± 0.006 Å. The angle taken with the nickel as the vertex between a nitrogen and the oxygen farthest from its averages 177 ± 2°, which is very close to the angle of 180° expected for octahedral coordination. The angle made between the planes of the two triangles infinitely extended is 179.5 ± 2°, so that they can be considered parallel.

The NiTRI complex is very inert with respect to hydrolysis by strong acids.[3] This could be accounted for by the positioning of the nitrogen atoms in the TRI ligand. The nitrogen atoms are all "turned up" toward the nickel. In this position they are effectively shielded from attack by protons from the rear by the large benzene rings and the nonbenzene carbons that are "turned down" below each of the turned up nitrogens. The nitrogens are similarly shielded on the other side by the nickel, two waters, and two nitrates that effectively block any possibility of attack from the front. Some idea of the shielding available can be had by constructing a model of the molecule using the Stuart and Briegleb models.

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Acetylacetone Complexes of Vanadium(II)

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Vanadium(II) forms mono, bis, and tris acetylacetone complexes; the formation constants in 1.00 *F* KCl are log $\beta_1 = 5.383$, log $\beta_2 = 10.189$, log $\beta_3 = 14.704$. These formation constants are compared with those for the acetylacetone complexes of all the other divalent ions of the first transition series. The vanadium(II) complex is an intense blue color, with $\epsilon_{\max}$ 2700 at 700 mμ. The standard potential for the oxidation of the tris complex to the vanadium(III) complex is +1.0 v. *vs.* n.h.e., indicating the vanadium(II) complex is a powerful reducing agent.

In the course of a survey of the properties of various complexes of vanadium(II), the acetylacetone (2,4-pentanedione) complex was prepared. Aqueous solutions of this complex were so intensely colored that a further study of the system seemed useful. This paper reports the results of spectrophotometric, potentiometric, and pH studies of the vanadium(II)–acetylacetone complexes. A least-squares method of computing complex ion stability constants is also described. A paper has appeared[1] reporting log β_1 and log β_2 values for these complexes in aqueous dioxane, but no other information was given. The present work was done in water solutions of ionic strength 1.00; in this medium a tris complex is formed, and values for all three stability constants have been obtained.

Experimental

Chemicals. Preparation of Vanadium(II) Solutions.—Reagent grade vanadium pentoxide was heated with excess concentrated hydrochloric acid until it appeared that all the vanadium was reduced to the +4 state. As much as possible of the excess acid was then evaporated off, and the solution was diluted with distilled water to give an acid solution of $VOCl_2$ of the desired concentration. This was placed in a cell and electrolyzed at a mercury cathode under a positive pressure of nitrogen until it appeared that all the vanadium was in the +2 state, and then for 30 min. longer; then it was transferred directly to a storage buret.[2] This method of preparation resulted in a solution containing only V^{2+}, H^+, and Cl^- ions. The V^{2+} content was determined by coulometric titration with bromine and the H^+ content by titration with ethylenediamine solution. The total vanadium content was determined by titration with potassium permanganate solution; the V^{2+} always accounted for at least 99.7% of the vanadium and any other species were ignored.

Other Chemicals.—Acetylacetone, Eastman White Label, was distilled within 24 hr. of its use. Ethylenediamine, practical grade, was used without further purification. The standard hydrochloric acid and sodium hydroxide were prepared from p-H Tamm ampoules (Chem-Tam, Sweden) and were checked by standard procedures; all other chemicals were reagent grade.

Instrumental.—Polarograms were recorded on a Sargent Model XV polarograph; the cell used was a conventional H-cell with a saturated calomel reference electrode. No special care was taken in measuring half-wave potentials; they are considered accurate to ±0.02 v.

The pH measurements were made with a Radiometer Model pHM 4c pH meter, a Beckman Type E-2 glass electrode, and a pressurized, carborundum-frit type saturated calomel electrode (Beckman). The electrode pair was used to measure hydrogen ion concentration as described previously, with an estimated precision of ±0.005 log [H^+] unit.[3] All equilibrium constants

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(1) J. M. Crabtree, D. W. Marsh, J. C. Tomkinson, R. J. P. Williams, and W. C. Fernelius, *Proc. Chem. Soc.*, 336 (1961).

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given are concentration quotients valid at 25°, $\mu = 1.00$.

In the titrations, base was added from a Manostat micropipet–buret, 1-ml. size. This could be read to 0.1 μl.; it was calibrated by delivering and weighing water or mercury. The maximum variation of any calibration was 0.4 μl. On this basis, the standard deviation of a single volume reading was taken as 1.0 μl.

Spectral Measurements.—The spectrum of the complex was recorded on a Cary Model 14 spectrophotometer; a Beckman DU spectrophotometer was used to make some of the absorbance measurements.

Results and Discussion

Stability Constants.—The method of Bjerrum[4] was used to obtain the formation function of the vanadium(II)–acetylacetone system. The first titrations of acidic solutions of vanadium(II) and acetylacetone with base gave pale yellow solutions, quite different from the intense blue color originally observed in qualitative experiments. This yellow compound could be extracted into ether, whereas the blue compound was completely insoluble in ether or carbon tetrachloride. It was concluded that the yellow color was caused by the vanadium(III)–tris(acetylacetone) complex which was being formed by oxidation. The oxidizing agent was found to come from the acetylacetone used; freshly distilled material did not cause oxidation, but after it had been standing for a week or so, it would become unsatisfactory. Only acetylacetone which had been distilled within 24 hr. of use was used thereafter.

The formation functions obtained from titrations in which there was about a 5:1 ratio of acetylacetone to vanadium reached a maximum at $\bar{n} = 2$, but the curves were not symmetric about $\bar{n} = 1$. Such asymmetry suggested that reactions other than complex formation were taking place. When the ratio of acetylacetone to vanadium was increased to 15 or 20:1, the formation functions leveled off at values of $\bar{n}$ between 2.2 and 2.7. Only when the ratio of acetylacetone to vanadium was made greater than 100:1 were the formation functions reproducible; at these ratios they clearly showed a 3:1 complex was being formed. The data reported here are taken from titrations in which the ratio of acetylacetone to vanadium was at least 100:1. A study of the hydrolysis of vanadium(II) is being undertaken in an attempt to interpret the data from the other titrations. Even at these high ligand/metal ratios it appears (as will be explained later) that the complexing reactions postulated do not fully represent the situation in the titration cell. In order to estimate the extent of hydrolysis in the titrations used, the value of the equilibrium constant for

$$V^{2+} + OH^- = VOH^+$$

must be known. This can be determined roughly by observing the pH of precipitation in a titration of vanadous ion with sodium hydroxide in the absence of any complexing agent (but see ref. 5). The titration curve obtained from a solution of 1.86×10^{-3} F vanadous chloride plus 1.4×10^{-2} F hydrochloric acid in 1 F potassium chloride showed no deviation from a typical strong acid–strong base curve up to pH 4.60. A deviation was observed at pH 4.80, and the solution changed color by pH 5.00. A precipitate was observed at pH 5.40. If one assumes at pH 4.60 no more than 1% of the vanadous ion has hydrolyzed, the maximum value for the hydrolysis constant can be calculated to be 1.5×10^7. On the other hand, if we assume that 10% has hydrolyzed by pH 4.80, the value of the constant is 9×10^6. Using the value of the first formation constant of the acetylacetone complex as reported in Table II and a value of 10^7 for the hydrolysis constant, we calculate that for the concentration of VOH^+ to be less than 1% of the concentration of $VAcac^+$, the ratio $[Acac^-]/[OH^-]$ must be greater than 4×10^3; this condition is met, for solutions with $[H^+] > 10^{-7}$, if the total acetylacetone concentration is greater than 5×10^{-2} F. Our experiments show definite hydrolysis when the acetylacetone concentration is 2×10^{-2} F, and even at 0.1 F the formation curves do not reach a maximum value of $\bar{n}$ of 3.0; the data reported are taken from titrations in solutions of 0.3 F acetylacetone.

The data obtained from two titrations which appeared uncomplicated by extraneous reactions are summarized in Table I, along with the values of $\bar{n}$ calculated from the derived stability constants which are listed in Table II. The values of $\bar{n}$ and $[Acac^-]$ in Table I were calculated as described earlier. The value of the acidity constant of acetylacetone used in these calculations was $1.325 \pm 0.015 \times 10^{-9}$ in 1.00 F KCl.[3] The value of pK_w was taken as 13.768 in 1.00 F KCl.[6] The stability constants were calculated from the data by a weighted least-squares procedure which is fully described in the Appendix to this paper. Weighted least-squares procedures for such calculations have been mentioned in the literature[7–9] and even described in some detail.[10–15] However, the important fact that the choice of a weighting system can be a subjective decision of the experimenter has not been emphasized, although it has been mentioned,[16,17] nor has the use of the χ parameter ("goodness of fit") been fully explained; for these reasons, it was felt that the least-squares

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Table I

Data Used in Calculating Formation Constants

Run A-9[‡]

ml NaOH added	-log $[H^+]$	-log $[Acac^-]$	$\bar{n}$	$\bar{n}_{Calc}$	$\Delta\bar{n}$
0	2.197	7.187	0.020	0.016	0.004
0.050	2.267	7.117	0.031	0.019	0.012
0.100	2.353	7.032	0.028	0.023	0.005
0.150	2.457	6.928	0.038	0.029	0.009
0.200	2.596	6.790	0.041	0.039	0.002
0.250	2.793	6.593	0.059	0.061	−0.002
0.300	3.112	6.275	0.119	0.123	−0.004
0.320	3.295	6.092	0.176	0.182	−0.006
0.330	3.395	5.992	0.219	0.225	−0.006
0.340	3.494	5.893	0.273	0.276	−0.003
0.350	3.594	5.794	0.335	0.337	−0.002
0.360	3.688	5.700	0.404	0.405	−0.001
0.370	3.775	5.613	0.480	0.478	0.002
0.380	3.857	5.531	0.559	0.556	0.003
0.390	3.933	5.456	0.642	0.636	0.006
0.400	4.009	5.380	0.728	0.725	0.003
0.420	4.139	5.251	0.902	0.897	0.005
0.440	4.255	5.135	1.081	1.071	0.010
0.460	4.371	5.020	1.261	1.261	0.000
0.480	4.471	4.921	1.444	1.434	0.010
0.500	4.572	4.820	1.627	1.615	0.012
0.520	4.674	4.719	1.810	1.796	0.014
0.540	4.790	4.604	1.993	1.994	−0.001
0.560	4.914	4.480	2.175	2.188	−0.013
0.580	5.049	4.346	2.356	2.371	−0.015
0.590	5.125	4.271	2.445	2.459	−0.014
0.600	5.212	4.184	2.533	2.548	−0.015
0.610	5.306	4.090	2.618	2.630	−0.012
0.620	5.423	3.974	2.699	2.713	−0.014
0.630	5.529	3.868	2.779	2.773	0.006
0.640	5.659	3.738	2.849	2.830	0.019
0.645	5.728	3.669	2.880	2.855	0.025
0.650	5.802	3.596	2.908	2.877	0.031
0.655	5.886	3.512	2.928	2.899	0.029
0.660	5.978	3.420	2.939	2.918	0.021
0.670	6.125	3.273	2.957	2.941	0.016
0.680	6.257	3.142	2.958	2.956	0.002
0.690	6.360	3.039	2.956	2.965	−0.009
0.700	6.446	2.953	2.951	2.972	−0.021
0.710	6.518	2.882	2.946	2.976	−0.030

Run A-10

ml NaOH added	-log $[H^+]$	-log $[Acac^-]$	$\bar{n}$	$\bar{n}_{Calc}$	$\Delta\bar{n}$
0	2.238	7.145	−0.117	0.016	−0.133
0.050	2.311	7.072	−0.078	0.019	−0.097
0.100	2.405	6.979	−0.070	0.024	−0.094
0.150	2.519	6.865	−0.040	0.031	−0.071
0.200	2.680	6.705	−0.026	0.044	−0.070
0.230	2.808	6.577	−0.004	0.059	−0.063
0.260	2.979	6.406	0.033	0.086	−0.053
0.290	3.220	6.166	0.100	0.145	−0.045
0.320	3.525	5.861	0.240	0.275	−0.035
0.330	3.625	5.761	0.307	0.336	−0.029
0.340	3.688	5.699	0.389	0.380	0.009
0.350	3.777	5.610	0.468	0.451	0.017
0.360	3.859	5.528	0.552	0.526	0.026
0.370	3.941	5.447	0.641	0.610	0.031
0.380	4.014	5.374	0.728	0.694	0.034
0.390	4.085	5.303	0.819	0.783	0.036
0.400	4.150	5.239	0.912	0.871	0.041
0.415	4.246	5.143	1.053	1.016	0.037
0.430	4.336	5.054	1.195	1.162	0.033
0.445	4.420	4.970	1.338	1.309	0.029
0.460	4.502	4.869	1.482	1.458	0.024
0.475	4.589	4.802	1.626	1.621	0.005
0.490	4.675	4.717	1.771	1.781	−0.010
0.500	4.729	4.663	1.867	1.880	−0.013
0.520	4.851	4.542	2.059	2.091	−0.032
0.540	4.986	4.407	2.250	2.298	−0.048
0.560	5.132	4.262	2.438	2.481	−0.043
0.580	5.305	4.090	2.621	2.645	−0.024
0.590	5.400	3.995	2.710	2.714	−0.004
0.600	5.508	3.887	2.793	2.777	0.016
0.605	5.571	3.825	2.832	2.806	0.026
0.610	5.640	3.756	2.868	2.835	0.033
0.615	5.717	3.679	2.900	2.862	0.038
0.620	5.789	3.607	2.930	2.883	0.047
0.625	5.869	3.527	2.953	2.903	0.050
0.630	5.945	3.451	2.973	2.919	0.054
0.635	6.032	3.365	2.982	2.933	0.049
0.640	6.102	3.295	2.992	2.943	0.049
0.645	6.167	3.230	2.999	2.951	0.048
0.650	6.226	3.171	3.004	2.958	0.046
0.660	6.323	3.074	3.015	2.966	0.049
0.670	6.414	2.984	3.013	2.972	0.041
0.680	6.490	2.908	3.009	2.977	0.032
0.690	6.558	2.840	2.999	2.980	0.019
0.700	6.618	2.781	2.987	2.983	0.004

[‡] Notes: Composition of Solutions. A-9, Moles of V(II): 1.064×10^{-4}, Moles of HAcac: 1.720×10^{-2}, Init. moles of HCl: 3.28×10^{-4}, Init. Vol: 52.0 ml, Conc. of NaOH: 1.001 F A-10, Moles of V(II): 1.011×10^{-4}, Moles of HAcac: 1.720×10^{-2}, Init. moles of HCl: 3.12×10^{-4}, Init. Vol.: 51.9 ml, Conc. of NaOH: 1.001 F

Table II

Formation Constants Calculated

	log β_1	log β_2	log β_3	χ
A-9	5.390 ± 0.009	10.209 + 0.008	14.712 ± 0.006	1.258
A-10	5.366 ± 0.009	10.138 ± 0.008	14.684 ± 0.007	3.293
Av. chosen	5.383 ± 0.012	10.189 ± 0.028	14.704 ± 0.014	...

procedure used here should be described and its application in other stability constant calculations pointed out.

The limits of error listed for each stability constant were obtained from the inverse matrix elements of the least-squares calculation in the usual manner; in order to do this, it is necessary to have the initial weights on an absolute scale, that is, to know the standard deviations of the experimentally measured quantities (see the Appendix). These quantities were obtained as explained in the Experimental section. The reported limits of error are valid only if there are no errors in any variables except pH and volume of titrant. Errors in standardizing the pH meter, or in the p*K* of acetylacetone, for example, would shift the entire formation function along the pAcac axis and cause the calculated formation constants to be wrong.

The "goodness of fit" parameter, χ, listed for both experiments reflects the agreement between the data and the calculated results. If the data agree within (approximately) their standard deviations with the calculated results, χ will be 1.0. If the agreement is within smaller tolerances, χ will be less than 1, and if the variation between data points and calculated points is greater than that predicted by the standard deviations, it will be greater than 1. Some workers[10] have used χ to estimate the errors in the input data to a least-squares calculation, *i.e.*, have adjusted the standard deviations of the data until a value of 1.00 is obtained for χ. While this is not wrong, it does not make full use of the information available from the least-squares procedure. If realistic estimates of the standard deviations *of the measured variables* are available, they should be used to calculate a value of χ; then, if the fit of the data to the theoretical curve is poor, an investigation as to possible causes can be undertaken. A good fit, on the other hand, gives additional evidence that the model chosen truly represents the reaction system.

This interpretation of χ is illustrated by using the data in Table I. For titration A-9, χ = 1.26 and the calculated formation curve fits the data visibly better than the curve for A-10 (χ = 3.29) fits its data (Figure 1). There was no essential difference in the two experiments. The same solutions, equipment, and

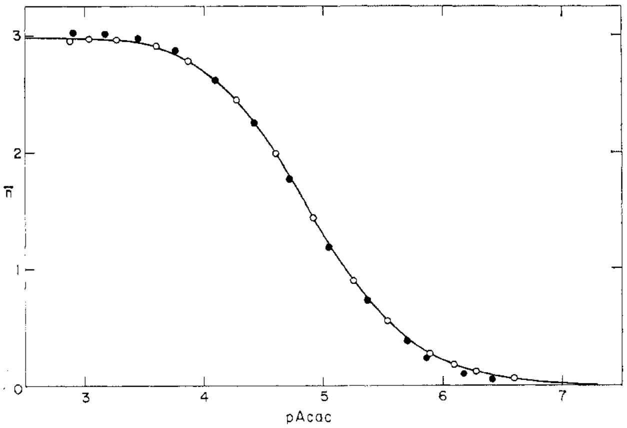

Figure 1.—Formation curve of vanadium(II)–acetylacetone: open circles, run A-9; dots, run A-10. The solid curve is drawn from the average constants obtained (see text).

glassware were used by the same person on the same day. Thus it would seem unreasonable to change the values of the standard deviations of measured pH and measured volume of titrant. On the other hand, *something* was wrong with A-10. This was first noticed in the values of $\bar{n}$, which were negative at the start of the titration and exceeded 3.0 at the maximum. We have not been able to find the error, but the high value of χ confirms its existence; in calculating the average formation constants, we have weighted the two sets of data as $1/\chi$ to take this goodness of fit into account. The standard deviations assigned to the average formation constants were obtained by considering both the standard deviations for each set of data and the agreement between the two sets.

As was mentioned earlier, even in the two titrations reported, there is some evidence that the experimental points cannot be fit perfectly by a three-parameter equation. This is evident from the column $\Delta\bar{n}$ in Table I, which shows that the theoretical curve seems to weave first above and then below the data points in trying to fit them. One would expect, if the errors in each point were random and the theoretical curve really could describe the data, that positive and negative deviations from this curve would appear more randomly. In fact, the general similarity of fit between A-9 and A-10 (positive and negative deviations appearing in bunches in the same relative ranges) convinces us that some species other than acetylacetone complexes are being formed; however, the over-all good fit of the data to the model, especially in A-9, is good evidence that the interferences are not of major importance. Hydroxy complexes of vanadium(II), or complexes of vanadium(III), are the most likely causes of the trouble.

The stability constants obtained in this study have one interesting feature: the third stability constant is larger than would be predicted on statistical grounds alone. Bjerrum has shown[4] that the ratio of the second formation constant to the first should be 0.208, and that of the third to the second 0.107. The ratios for vanadium(II)–acetylacetone complexes are, respectively, 0.265 and 0.551; the addition of ligands appears to be more favored than one would predict statistically. It is not easy to rationalize this, considering the relatively bulky groups which are being attached, but the fact that the total charge on the system never exceeds −1 may be a helping factor.

A second point of interest in connection with vanadium(II) complexes is their relative lability. The electronic configuration of the vanadous ion is d^3, the same as chromium(III), and therefore substitution reactions of vanadium(II) might be expected to proceed relatively slowly. No evidence for this was seen: in solutions where no hydroxide precipitate was observed, the addition to base or acid resulted in immediate changes in pH to within 0.005 pH unit of the final value, and if a color change accompanied the pH change, it appeared to take place instantaneously. Several attempts were made to form the complex in basic solution and then titrate it with acid, thereby approaching the equilibrium from the opposite direction. These attempts were unsuccessful, in that the vanadium(II) complex appeared to be oxidized by the added hydrogen ion, and no formation curves could be obtained to verify the establishment of equilibrium.

With the stability constants for vanadium(II) known, one can compare the values of such constants for all the divalent cations of the first transition series (Figure 2). This comparison was intended to be as uniform as possible, and therefore values for the later metal ions were all taken from one set of papers[18]; still, there are differences in ionic strength (1.00 and 0) and temperature (25.0 and 30.0°) between the results for vanadium and chromium and the rest of the elements. Nevertheless, it is clear that the early and late members of the transition series both follow the same pattern, *i.e.*, that of increasing stability with increasing ligand field stabilization,[19] and that differences in behavior are quantitative rather than qualitative. Both chromium and copper form more stable complexes than one would guess, with copper deviating more. However, the earlier statement[1] that the complex of vanadium(II) with acetylacetone is of the same stability as the complex of copper(II) seems not to be borne out; the effect observed earlier is probably due to differences in solvent used (water *vs.* 50% dioxane).

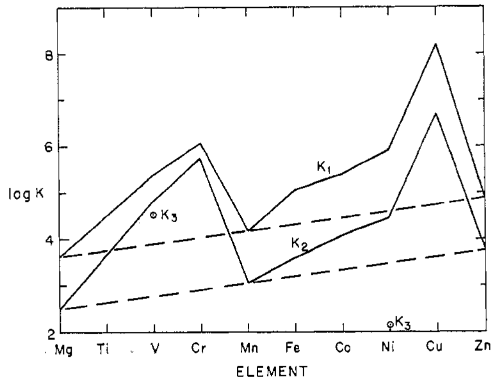

Figure 2.—Stability constants of acetylacetone complexes. Mg(II) was chosen rather than Ca because its radius is nearer that of the transition elements, μ = 0, 30.0°; Ti(II) is not known in aqueous solution; V(II), this work, μ = 1.00, 25.0°; Cr(II), ref. 6, μ = 1.00, 25.0°; Mn(II), ref. 18, μ = 0, 30.0°; Fe(II), ref. 18, μ = 0, 30.0°; Co(II), ref. 18, μ = 0, 30.0°; Ni(II), ref. 18, μ = 0, 30.0°; Cu(II), ref. 18, μ = 0, 30.0°; Zn(II), ref. 18, μ = 0, 30.0°.

Spectral Studies.—As noted above, it was the intense blue color of the vanadium(II)–acetylacetone complex which originally attracted attention and the system was first investigated with a view to using this color in an analytical procedure for vanadium or acetylacetone; this hope was not fulfilled.

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(18) (a) R. M. Izatt, C. G. Haas, Jr., B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, **58**, 1133 (1954); (b) R. M. Izatt, W. C. Fernelius, and B. P. Block, *ibid.*, **59**, 80 (1955); (c) R. M. Izatt, W. C. Fernelius, and B. P. Block, *ibid.*, **59**, 235 (1955).

(19) L. E. Orgel, "Transition Metal Chemistry," Methuen, London, 1960.

The spectrum from 400 to 1350 mμ of a basic solution of vanadium(II) with a large excess of acetylacetone shows a broad band with $\lambda_{\max}$ at 700 mμ ($\epsilon_{\max}$ 2700). There is a small peak at about 450 mμ ($\epsilon_{\max}$ ~500). The absorbance at the 700 mμ peak is roughly linear with concentration, but the straight line does not go through the origin. This is attributed to oxidation of the vanadous complex to a vanadium(III) species; the absorbance at the peak can be observed to decrease slowly no matter how carefully the solutions are prepared. This decrease amounts to as much as 10% in the first hour after mixing, and for this reason no effort was made to develop an analytical method using the complex. When a solution, initially dark blue, is deliberately oxidized, only a yellow color remains and the absorbance at 700 mμ goes to zero. The vanadium species in such a solution was determined by polarography to be vanadium(III).

The absorbance of the vanadous complex is higher than normally found for transition metal ions and also much higher than the absorbances of the acetylacetone complexes of any of the other divalent first-row transition metal ions. The possibility that the color was due to a mixed-valence compound [some compound of vanadium(II) and vanadium(III), the vanadium(III) having been formed by oxidation] was considered,[20] but ruled out when it was shown that deliberate oxidation caused a decrease in absorbance; moreover, in carefully-prepared solutions over 98% of the vanadium could be found in the +2 state if the solution was titrated immediately after mixing. The absorbance is then either a very strong Laporte-forbidden band, or a very weak charge-transfer band[21]; its existence may be of interest to a theoretician. The weaker band at 450 mμ seems to be associated with the vanadium(II) also, because it too disappears when the vanadium is oxidized. No measurements were made below 400 mμ, because the acetylacetone begins to absorb very strongly there. Basic solutions of acetylacetone are transparent down to 350 mμ, but the tail of the absorbance is moved up to 400 mμ upon addition of vanadium.

Polarography.—In view of the rapid self-oxidation of the solutions prepared for the spectrophotometric studies, it seemed useful to determine the potential for the reaction

$$V(Acac)_3^- \longrightarrow V(Acac)_3 + e^-$$

In 1 *F* potassium chloride solutions at pH 12, a fairly well-developed anodic wave is obtained from vanadium(II)–acetylacetone with a half-wave potential of −1.25 v. *vs.* s.c.e. The diffusion current constant, *i.e.*, $i_d/cm^{2/3}t^{1/6}$, in such a solution is −1.2, roughly comparable to those found by Lingane and Meites for other vanadium(II) complexes in basic media.[22]

When such a solution is oxidized, a cathodic wave is found for the reverse of the reaction above, with $E_{1/2}$ = −1.31 v. *vs.* s.c.e. Thus the standard potential for the reaction is +1.0 v. *vs.* the hydrogen electrode, and the notion that the vanadous complex is a good reducing agent is confirmed.

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Appendix

The Method of Least Squares.—The mathematical basis for this method has been described and developed by many writers: Deming,[23] Rydberg,[9] and Sullivan, *et al.*,[10] are good sources of further references. The discussion here is confined to the problem of determining from pH measurements the values of β_1, β_2, and β_3 for coordination of a monobasic ligand HL with a metal ion M, where

$$\beta_i = \frac{[ML_i]}{[M][L]^i} \tag{1}$$

(All charges are omitted for simplicity.) The extension to more complicated systems is straightforward. The basic equation we have is

$$\sum_i \beta_i(\bar{n} - i)[L]^i = 0 \qquad (\beta_0 \equiv 1) \tag{2}$$

i.e.

$$\beta_3(\bar{n} - 3)[L]^3 + \beta_2(\bar{n} - 2)[L]^2 + \beta_1(\bar{n} - 1)[L] + \bar{n} = 0 \tag{3}$$

The quantities $\bar{n}$ and [L] are calculated at each point in a titration; since there are 10–50 points available, the system is overdetermined, and this is why a least-squares method is particularly suitable.

The principle of a least-squares calculation is plain: one seeks a set of β values which minimizes the sum of the squares of the differences between the observed and the calculated values. The difficulty arises in this case because the observed values are pH and volume, the results are plotted as $\bar{n}$ *vs.* pL, and the equation connecting these is in terms of [L] itself. It is this last conversion which is especially critical; whereas the variable pL covers a range of only 2 to 8 say, the value of [L] changes by six orders of magnitude, and a proper choice of weights for each point must allow for this variation.

There are two general ways of using the method. In either case, a preliminary set of β values is guessed (most easily by using values of pL at half-integral values of $\bar{n}$); then either a new set of β values or a set

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[20] N. Davidson, private communication.

[21] T. M. Dunn in J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y., 1960, p. 279.

[22] J. J. Lingane and L. Meites, *J. Am. Chem. Soc.*, **73**, 2165 (1951).

[23] W. E. Deming, "Statistical Adjustment of Data," John Wiley and Sons, New York, N. Y., 1943.

of corrections to the original β values is obtained from a least-squares cycle. The calculation is repeated until a cycle results in no change in the β values. The first method was used here; a maximum of four cycles was required for convergence in any case. We take eq. 3 and rewrite it as

$$A_3\beta_3 + A_2\beta_2 + A_1\beta_1 + A_0 = 0 \qquad (4)$$

where $A_i = (\bar{n} - i)[\mathrm{L}]^i$. For each experimental point we can calculate a value of $\bar{n}$ and of [L], and therefore a value of A_0, A_1, A_2, and A_3. In the least-squares procedure, we wish to make

$$\Sigma w(A_3\beta_3 + A_2\beta_2 + A_1\beta_1 + A_0)^2 = \text{minimum} \qquad (5)$$

where the sum is taken over all the data points. The weight w chosen for each point should be inversely proportional to the absolute error associated with that point. Here we are taking about each point ($\bar{n}$, [L]), with possible errors in each of the two quantities. We know that if there were no errors in $\bar{n}$ or [L], the function

$$F = (\bar{n} - 3)\beta_3[\mathrm{L}]^3 + (\bar{n} - 2)\beta_2[\mathrm{L}]^2 + (\bar{n} - 1)\beta_1[\mathrm{L}] + \bar{n} \qquad (6)$$

would equal zero. Therefore, to take into account errors in both $\bar{n}$ and [L], we take the weight for each point as

$$w = \frac{1}{\sigma^2 F} \qquad (7)$$

where σF is the standard deviation in a measured value of F. (This appoach is similar to that used by Hugus.[17]) From the form of F, this standard deviation can be written as

$$\sigma^2 F = \left(\frac{\partial F}{\partial[\mathrm{L}]}\right)^2 \sigma^2[\mathrm{L}] + \left(\frac{\partial F}{\partial \bar{n}}\right)^2 \sigma^2\bar{n} \qquad (8)$$

Several attempts were made to use this as a weighting function, getting the required derivatives from eq. 3 and guessing at the standard deviations in $\bar{n}$ and [L], but the fit of the calculated formation curves to the data was never very good. Therefore, since good estimates of the standard deviations of the experimental measurements themselves were available, the weighting function was rewritten to use them

$$\sigma^2 F = \left[\left(\frac{\partial F}{\partial[\mathrm{L}]}\right)\left(\frac{\partial[\mathrm{L}]}{\partial \mathrm{pH}}\right) + \left(\frac{\partial F}{\partial \bar{n}}\right)\left(\frac{\partial \bar{n}}{\partial \mathrm{pH}}\right)\right]^2 \sigma^2\mathrm{pH} + \left[\left(\frac{\partial F}{\partial[\mathrm{L}]}\right)\left(\frac{\partial[\mathrm{L}]}{\partial V}\right) + \left(\frac{\partial F}{\partial \bar{n}}\right)\left(\frac{\partial \bar{n}}{\partial V}\right)\right]^2 \sigma^2 V \qquad (9)$$

where V is the volume of titrant used. This expression relates the weight to the errors in the measured variables as it should be.

($\partial F/\partial[\mathrm{L}]$) and ($\partial F/\partial\bar{n}$) are obtained by direct differentiation of eq. 3.

$$\frac{\partial F}{\partial[\mathrm{L}]} = 3\beta_3(\bar{n} - 3)[\mathrm{L}]^2 + 2\beta_2(\bar{n} - 2)[\mathrm{L}] + \beta_1(\bar{n} - 1) \qquad (10)$$

$$\frac{\partial F}{\partial \bar{n}} = \beta_3[\mathrm{L}]^3 + \beta_2[\mathrm{L}]^2 + \beta_1[\mathrm{L}] + 1 \qquad (11)$$

($\partial[\mathrm{L}]/\partial\mathrm{pH}$) and ($\partial\bar{n}/\partial\mathrm{pH}$) can also be obtained analytically as follows: We have the two equations

$$[\mathrm{L}] = \frac{K_1}{K_1 + [\mathrm{H}^+]}(\Sigma_\mathrm{L} - \bar{n}\Sigma_\mathrm{M}) \qquad (12)$$

and

$$\bar{n} = \frac{K_1 + [\mathrm{H}^+]}{[\mathrm{H}^+]\Sigma_\mathrm{M}}\left\{[\mathrm{H}^+] + 2\Sigma_\mathrm{M} + [\mathrm{Na}^+] - \frac{K_\mathrm{w}}{[\mathrm{H}^+]} - [\mathrm{Cl}^-] - \frac{K_1}{K_1 + [\mathrm{H}^+]}\Sigma_\mathrm{L}\right\} \qquad (13)$$

where Σ_M is the total concentration of metal ion, Σ_L is the total concentration of ligand, and K_1 is the acidity constant of the ligand. Differentiating and rearranging these gives

$$\frac{\partial[\mathrm{L}]}{\partial[\mathrm{H}^+]} = -\frac{K_1}{[\mathrm{H}^+]}\left\{1 + \frac{K_\mathrm{w}}{[\mathrm{H}^+]^2} + \frac{[\mathrm{L}]}{K_1}\right\} \qquad (14)$$

$$\frac{\partial \bar{n}}{\partial[\mathrm{H}^+]} = \frac{K_1 + [\mathrm{H}^+]}{[\mathrm{H}^+]\Sigma_\mathrm{M}}\left\{1 + \frac{K_\mathrm{w}}{[\mathrm{H}^+]^2} + \frac{K_1\Sigma_\mathrm{L}}{(K_1 + [\mathrm{H}^+])^2}\right\} - \frac{K_1\bar{n}}{[\mathrm{H}^+](K_1 + [\mathrm{H}^+])} \qquad (15)$$

and these can be converted to the desired derivatives using the relation

$$d[\mathrm{H}^+] = -2.3[\mathrm{H}^+]\,d\mathrm{pH} \qquad (16)$$

No method was found to obtain expressions for $\partial[\mathrm{L}]/\partial V$ or $\partial\bar{n}/\partial V$, however, so these derivatives had to be evaluated numerically. The calculation of $\bar{n}$ and [L] from each set of data points (pH, V) was made correctly, and then repeated using ($V + \Delta V$) in place of V. This gave new values of $\bar{n}$ and [L], and the derivatives were calculated at each point. For the system discussed here, these values were rather constant over the whole range of pH values, but they will vary if the pH approaches the pK of a ligand.

We now take the weights calculated for each point and write the matrix equation for the least-squares calculation

$$\begin{pmatrix} \sum_j w_j(A_{33})_j & \sum_j w_j(A_{32})_j & \sum_j w_j(A_{31})_j \\ \sum_j w_j(A_{23})_j & \sum_j w_j(A_{22})_j & \sum_j w_j(A_{21})_j \\ \sum_j w_j(A_{13})_j & \sum_j w_j(A_{12})_j & \sum_j w_j(A_{11})_j \end{pmatrix} \begin{pmatrix} \beta_3 \\ \beta_2 \\ \beta_1 \end{pmatrix} = \begin{pmatrix} -\sum_j w_j(A_{30})_j \\ -\sum_j w_j(A_{20})_j \\ -\sum_j w_j(A_{10})_j \end{pmatrix} \qquad (17)$$

or

$$\mathbf{A}\boldsymbol{\beta} = \boldsymbol{A}$$

where again the sums are taken over all the data points.

(The symbol A_{32}, for example, means $A_3 \times A_2$, the A_i values being those of eq. 4.) This equation is solved for the β values by inverting the matrix **A** and multiplying A by $\mathbf{A}^{-1}$. One manipulative detail which may be troublesome is that the matrix elements cover a wide range of values—in the work reported here, 10^{-31} to 10^{-9}—and the weights may have to be multiplied by some constant to keep the numbers within the capacity of the computer used. This constant can be factored out later.

The least-squares procedure gives not only a set of β values but also their standard deviations *if the weights are on an absolute basis, i.e.*, if the terms in eq. 9 are all known and the proper estimates of σpH and σV are used. If this is done, the standard deviations of the β values are equal to the square roots of the corresponding diagonal elements of the inverse matrix [*i.e.*, $\sigma\beta_3 = (A_{33}^{-1})^{1/2}$].

The last information available is the "goodness of fit," χ, described in the text. This is calculated by evaluating F (eq. 6) at each point ($\bar{n}$, [L]) using the calculated β values. These quantities are called the residuals; they would be zero if there were no errors in $\bar{n}$, [L], or the β values. The residual at each point is multiplied by the weight calculated for that point; then

$$\chi = \sqrt{\frac{\Sigma w \times (\text{residual})^2}{N}} \qquad (18)$$

where N is the number of observations (number of points) minus the number of parameters determined (3 in this case: β_1, β_2, and β_3). The interpretation of χ is described in the text.

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Difluoramine: an Infrared Study of the Complexes between Difluoramine and the Alkali Metal Fluorides

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Difluoramine, HNF_2, was condensed on alkali metal fluoride optical crystals, and the infrared spectra of the resulting compounds were measured. Complex formation was observed with KF, RbF, and CsF. An analysis of the infrared spectra indicates that two compounds may be formed, one a simple hydrogen bonded complex, and the other a new species $MNF_2 \cdot HF$.

Introduction

Potassium, rubidium, and cesium fluorides form complexes with difluoramine (that dissociate reversibly) when the latter is condensed onto these materials. When the potassium and rubidium complexes are allowed to warm to room temperature they react further to form the *cis* and *trans* difluorodiazine isomers and the alkali metal bifluorides. The cesium complex explodes before reaching room temperature.[1]

It has been postulated that the explosive nature of the cesium complex as contrasted with the nonexplosive nature of the potassium and rubidium complexes might be due to the formation of difluoramide ion, NF_2^-. The present infrared study of the structures of these complexes was undertaken with the purpose of determining whether such an ion does exist.

Infrared spectra of the complexes were obtained by condensing difluoramine onto optical blanks of the alkali metal fluorides at −95° and scanning through the rock salt region with a Beckman IR-7 spectrometer. Examination of the spectra indicates that potassium and rubidium fluorides primarily form hydrogen-bonded complexes of the structure $M^+F^- \cdot HNF_2$ with possible small amounts of a difluoramide complex, $M^+ \cdot FH \cdot NF_2^-$, also present. Cesium fluoride seems at first to form a complex with two (or more) moles of difluoramine. On pumping this is converted to a mixture of $Cs^+F^-H \cdot NF_2$ and $Cs^+ \cdot FH \cdot NF_2^-$. The evidence for the existence of a difluoramide ion is strongest in the case of cesium.

Experimental

The difluoramine was prepared by the action of concentrated sulfuric acid on fluorinated urea. It was then purified by distillation under vacuum at reduced temperatures.[2] The potassium and cesium fluoride crystals were obtained from the Harshaw Chemical Co. and the rubidium fluoride from Semi-Elements, Inc.

The alkali fluoride single crystal was mounted on a copper block inside an infrared cell fitted with rock salt windows. Gaseous difluoramine was condensed onto a 1 × 1 in. optical blank of the appropriate alkali metal fluoride maintained at about −95° by a slush bath of methylcyclohexane. The copper block was in contact with the slush coolant so that the alkali fluoride plates could be kept at the proper temperature, which was meas-

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(1) E. A. Lawton, D. Pilipovich, and R. D. Wilson, U. S. Patent 3,109,711 (Nov. 5, 1963).

(2) E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **81**, 4755 (1959); E. A. Lawton and D. F. Sheehan unpublished work.