Thermodynamics of Coordination to an Unsolvated Position in Vanadyl Acetylacetonate

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The enthalpy change for the reaction of a number of nitrogen and oxygen donors with vanadyl acetylacetonate has been measured calorimetrically in nitrobenzene solution; the measured values span the range from -10.59 ± 0.35 to -5.77 ± 1.23 kcal./mole for n-decylamine and methanol, respectively. The equilibrium constants for the reaction are found to lie between ≥ 1000 and 0.55 ± 0.15 l./mole for the same substances. Both steric effects and inductive effects are found to affect the heat of the reaction, but the results show that vanadyl acetylacetonate is not a sensitive indicator of relative base strength. Several measurements with vanadyl trifluoroacetylacetonate give a quantitative measure of the inductive effect in the chelate ring.

The effect of solvation of the sixth position in the coordination sphere of vanadyl bis(acetylacetonate), $VO(acac)_2$, is known[1-3]; the transition[4] from $^2B_2$ to $^2E(I)$ shifts to lower energy. When $VO(acac)_2$ is allowed to react with bases in a noncoordinating solvent, this spectral change affords a method for the determination of the equilibrium constant of adduct formation. Since solvation of the sixth position is small in both benzene and nitrobenzene, the solvents which have been used for these measurements, the thermodynamic functions obtained are essentially those for an addition reaction, rather than a replacement reaction. The system then serves as a convenient method for the determination of relative base strength in a nonhydrogen-bonding medium.

We take the enthalpy change, $\Delta H°$, of the reaction as one measure of base strength. Temperature variation of the equilibrium constant allows a measurement of $\Delta H°$, but since the accuracy of the spectrophotometric measurements is low, we have also measured the enthalpy changes directly by calorimetry.

There has been some discussion in the literature[5] concerning the delocalization in the acetylacetonate chelate ring. We have found that the trifluoroacetylacetonate chelate of vanadyl ion also serves as a reference acid; this allows a measurement of the effect of substitution in the chelate ring on the acceptor behavior of the vanadium atom.

Experimental

Vanadyl acetylacetonate was prepared as described in the literature[6] and recrystallized from benzene.

$VO(TFACA)_2$, the trifluoroacetylacetonate chelate, was prepared by dissolving 46 g. of $VOSO_4 \cdot 2H_2O$ in 25 ml. of H_2O and 2.5 ml. of concentrated H_2SO_4, adding 100 g. of HTFACA, neutralizing with Na_2CO_3 to pH 6, filtering, and washing with two 15-ml. portions of benzene to remove excess ligand. The product was dried over sulfuric acid and recrystallized twice from benzene. The over-all yield was about 27%, m.p. 228–231° dec. *Anal.* Calcd. for $VC_{10}H_8O_5F_6$: V, 13.68; C, 32.20; H, 2.15. Found: V, 13.67; C, 32.48; H, 2.33. Analysis was by Alfred Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mülheim, West Germany.

The nitrobenzene was distilled shortly before use, and all amines were distilled from zinc dust. The methanol (Mallinckrodt analytical reagent grade), triphenylphosphine oxide (m.p. 155–157°, K and K Laboratories), and hexamethylphosphoramide (Aldrich Chemical Co.) were used without further purification.

Apparatus and Procedure. The stability constants, $K = [\text{complex}]/[VO(acac)_2][\text{base}]$, were determined spectrophotometrically, since the visible band is shifted about 1000 Å. to lower energy on coordination of the base. $VO(acac)_2$ was weighed into 10-ml. volumetric flasks and partially diluted with nitrobenzene. Then a known amount of base was added using Lambda micropipets and the solution diluted to 10 ml. The spectra of these solutions were immediately recorded on a Cary 14 spectrophotometer from 12,000 to 6000 Å. The cell compartment was thermostated at room temperature to prevent heating by the infrared lamp. The temperature of each solution was measured during the time that the spectrum was recorded by means of a thermocouple inserted in the silica cell through the ground-glass top. The extinction coefficient of $VO(acac)_2$ in nitrobenzene was determined readily, and that of the adduct was determined, in most cases, by adding a large excess of the base to a $VO(acac)_2$ solution in nitrobenzene. Where this was not sufficient to cause complete coordination, the extinction coefficient of the complex was determined by trial and error using the value which gave the most reproducible K. The equation used for calculation of the stability constants was

$$K = \frac{\left(\dfrac{A - A_0}{\epsilon_c - \epsilon_v}\right)}{\left\{[VO(acac)_2]_0 - \left(\dfrac{A - A_0}{\epsilon_c - \epsilon_v}\right)\right\}\left\{[\text{base}]_0 - \left(\dfrac{A - A_0}{\epsilon_c - \epsilon_v}\right)\right\}}$$

where A = measured absorption at the chosen wave length, A_0 = calculated absorption at the wave length in the absence of base ($A_0 = \epsilon_v[VO(acac)_2]_0$), and

(1) R. D. Feltham, University of California Report, UCRL-3867.
(2) I. Bernal and P. H. Rieger, *Inorg. Chem.*, **2**, 256 (1963).
(3) D. Kivelson and S. K. Lee, *J. Chem. Phys.*, **41**, 1896 (1964).
(4) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
(5) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962); D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); J. P. Collman, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963.
(6) R. A. Rowe and M. M. Jones, *Inorg. Syn.*, **5**, 114 (1957).

Table I. Spectral Data for Adducts in Nitrobenzene Solution

Ligand	ν_1, cm.$^{-1}$	ϵ_1, M^{-1} cm.$^{-1}$	δ_1,[a] cm.$^{-1}$	ν_2, cm.$^{-1}$	ϵ_2, M^{-1} cm.$^{-1}$	δ_2,[a] cm.$^{-1}$
Methanol[b]	12880	38.0	1710	17530	8	1610
Triphenylphosphine oxide	12820	44.2	1160	17020	11	2400
Hexamethylphosphoramide	12620	46.0	1200	16880	14	2310
Pyridine	13010	35.6	1620	17450	19	1270
3-Picoline	13000	41.2	1610	17420	23	1220
4-Picoline	13000	39.7	1610	17420	22	1270
3,5-Lutidine	12990	42.2	1660	17420	23	1240
3,4-Lutidine	12960	40.1	1620	17450	23	1260
2,6-Lutidine	13050	39.1	1590	17420	23	1220
Quinoline[b]	13100	45.5	1500	17440	24	1430
Morpholine	12990	32.0	1540	17390	24	1580
Pyrrolidine	12950	33.2	1480	17390	27	1580
Piperidine[c]	13030	36.5	1560	17320	23	1460
2-Methylpiperidine[c]	13280	36.6	1680	17860	53	2110
Diethylamine[c]	13090	30.7	1520	17390	27	1520
Dibutylamine[c]	13230	32.4	1670	17570	28	2030
n-Butylamine	12990	32.3	1430	17350	23	1380
n-Decylamine	12990	32.1	1520	17390	23	1420
Nitrobenzene[b]	14780	53.7	1650	17090	24	880
VO(TFACA)$_2$ in nitrobenzene	14280	46.9	1910	17170	18	930
VO(TFACA)$_2$ + pyridine in nitrobenzene	13580	41.5	1760	17480	26	1300

[a] Band half-width at half-height.   [b] Ligand used as solvent.   [c] Obvious decomposition took place.   A rough correction was made.

[VO(acac)$_2$]$_0$ and [base]$_0$ = initial concentrations of the two species. The resulting K values were then averaged and the standard deviation calculated. Then, knowing $\Delta H°$ for the reaction and the temperature at which K was determined, K_{298} could be calculated.

The calorimeter used in this work was identical with those used in calorimetric studies involving the boron halides[7,8] and the phosphorus halides.[9] It was constructed by the Ace Glass Co. from a copy of the original design, kindly furnished us by Dr. R. R. Holmes. A diagram of the apparatus, the method of the preparation of the solutions, and the general operational procedure have appeared elsewhere.[7-9] The constant temperature bath was maintained at 25.25° over the time period of the measurements. A calorimeter thermometer, 18 to 31°, graduated in 0.01° divisions, was used to measure the temperature rise. The electrical calibration details were similar to standard procedures.[10]

In most cases it was necessary to have the base 10 to 100 times as concentrated as the VO(acac)$_2$ in order to ensure complete coordination, so a blank correction for dilution of the excess base was necessary for each system. The results reported are based on at least three runs in every case.

Our procedures yielded $\Delta H = -13.5 \pm 0.3$ kcal./ mole for the neutralization of perchloric acid with sodium hydroxide. This may be compared with the accepted value, $\Delta H = -13.4 \pm 0.02$ kcal./mole,[11] at the same ionic strength.

Results

The spectral data for the first two bands of the ad-

(7) H. C. Brown and R. H. Horowitz, *J. Am. Chem. Soc.*, **77**, 1730 (1955).
(8) H. C. Brown and R. R. Holmes, *ibid.*, **78**, 2173 (1956).
(9) R. R. Holmes, W. P. Gallagher, and R. P. Carter, Jr., *Inorg. Chem.*, **2**, 437 (1963).
(10) W. P. Gallagher, Ph.D. Thesis, Carnegie Institute of Technology, 1961.
(11) J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, **67**, 2605 (1963).

ducts are summarized in Table I; allowance has been made, where necessary, for band overlap.

A typical set of data for the reaction in benzene solution is illustrated in Figure 1. It will be noted that the inaccuracy in the equilibrium constants is due in part to the relatively small change in extinction coefficient observed at any given wave length when either benzene or nitrobenzene is used as solvent. A sharp isosbestic point is observed in either solvent, which is consistent with our hypothesis that there are two absorbing species, VO(acac)$_2$ and VO(acac)$_2$-B, in solution. The spectrum of VO(acac)$_2$-B in pure base as solvent did not pass through the isosbestic point, however; it fell below the isosbestic point in benzene and above that in nitrobenzene. This suggests to us a small dielectric constant effect on the spectra, which is not too surprising when the dipolar nature of the vanadium–vanadyl oxygen bond is considered.

It was originally thought that ΔH values could be obtained from stability constants measured at different temperatures, using benzene as a solvent. As Table II shows, the relatively large errors in K caused large uncertainties in ΔH. These large errors in K are due to three effects: (1) problems with decomposition in the cases of piperidine, pyrrolidine, and aliphatic amines in general; (2) the small change in extinction coefficients referred to above; and (3) evaporation and concentration changes due to the volatility of benzene. This latter problem was also encountered when direct calorimetric measurements were made; an approximate value for the VO(acac)$_2$-pyridine system is $\Delta H = -7.1 \pm 0.9$ kcal./mole in benzene. The use of nitrobenzene as solvent reduced the experimental error greatly, giving the better result, $\Delta H = -7.35 \pm 0.19$ kcal./ mole. The close agreement between the equilibrium constants measured in these two solvents (see Tables II and III) indicates that solvation effects in nitrobenzene and benzene are similar. Therefore, the direct calorimetric measurements were done in nitrobenzene solution. The results are shown in Tables III and IV.

Table II. Representative Data for the Association Reaction with VO(acac)$_2$ in Benzene

Ligand	Temp., °C.	K, l./mole	$-\Delta H$, kcal./mole
Pyridine	25.0	56 ± 5	
	28.5	46 ± 3	8 ± 1
	37.0	30 ± 4	
	46.5	24 ± 4	
Piperidine	25.0	1400 ± 300	
	28.5	1100 ± 100	11 ± 1
	37.0	720 ± 180	
	46.5	410 ± 20	
Pyrrolidine	25.0	2900 ± 1000	
	28.5	2100 ± 800	13 ± 4
	37.0	1010 ± 70	
	46.5	820 ± 110	
2-Methylpiperidine	27.6	13 ± 2	
Dibutylamine	28.0	22 ± 7	
Diethylamine	28.2	14 ± 4	

Table V. It is evident that there is some variation in ΔH_{dil} with concentration for these substances, but the variations are much smaller than the experimental errors in the measured over-all heat of reaction. Therefore, if it is assumed that the ΔH_{dil} of VO(acac)$_2$ and the adduct are also small, then the measured ΔH may be called $\Delta H°$, within the accuracy of the measurement. With $\Delta G°$ and $\Delta H°$ in hand, we are then able to obtain $\Delta S°$ by simple arithmetic, but the accuracy in $\Delta S°$ is not great enough, even among the pyridines, to make many interesting correlations.

There are two ways to assign relative base strengths in a donor–acceptor reaction such as the one being considered here. The first uses the enthalpy change of the reaction, according to the school of H. C. Brown, and this is why we have measured the heats calorimetrically. Several trends are then immediately ap-

Table III. Thermodynamic Quantities for the Association Reaction in Nitrobenzene at 25°[a]

Ligand	$-\Delta H°$, kcal./mole	K, l./mole	$-\Delta G°$, kcal./mole	$-\Delta S°$, e.u.[b]
Pyridine	7.35 ± 0.19	58.0 ± 4.0	2.40 ± 0.04	16.6 ± 0.7
3-Picoline	8.10 ± 0.21	65.4 ± 5.9	2.47 ± 0.05	18.9 ± 0.9
4-Picoline	8.80 ± 0.23	139.7 ± 10.6	2.92 ± 0.04	19.7 ± 0.9
3,5-Lutidine	6.76 ± 0.43	103.2 ± 8.8	2.74 ± 0.05	13.5 ± 1.6
3,4-Lutidine	7.31 ± 0.08	135.2 ± 17.5	2.90 ± 0.08	14.8 ± 0.5
2,6-Lutidine	7.36 ± 0.25	6 ± 1	1.06 ± 0.1	21.2 ± 1.2
Quinoline	4.83 ± 0.20	1.86 ± 0.23	0.36 ± 0.07	15.0 ± 0.9
Pyrrolidine	10.47 ± 0.21	⩾1000		
Morpholine	9.34 ± 0.24	300 ± 150	3.38 ± 0.31	20.0 ± 1.9
Piperidine	10.06 ± 0.33	1000 ± 200	4.09 ± 0.14	20.0 ± 1.6
2-Methylpiperidine	7.69 ± 0.34	19.2 ± 4.0	1.75 ± 0.13	19.9 ± 1.6
Diethylamine	9.50 ± 0.50	10 ± 5	1.36 ± 0.41	27.3 ± 3.1
Di-n-butylamine	9.75 ± 0.45	12 ± 5	1.47 ± 0.31	27.8 ± 2.6
n-Butylamine	10.42 ± 0.17	⩾1000		
n-Decylamine	10.59 ± 0.35	⩾1000		
Methanol	5.77 ± 1.23	0.55 ± 0.15	−0.35 ± 0.19	20.6 ± 4.8
Triphenylphosphine oxide	5.91 ± 0.14	31.6 ± 5.5	2.04 ± 0.11	13.0 ± 0.8
Hexamethylphosphoramide	5.93 ± 0.49	105.2 ± 22.2	2.75 ± 0.13	10.7 ± 2.1

[a] Errors expressed as standard deviation.   [b] Errors in this column are derived, not experimental.

Where possible the equilibrium constants were also measured in nitrobenzene solution. It was not possible in the VO(TFACA)$_2$–B reactions because of the small change in the spectrum, and in those VO(acac)$_2$–B reactions where the base is an aliphatic amine only an approximate value is given because of decomposition. Although some decomposition also takes place during the calorimetric measurements, the temperature extrapolation method used cancels it out to a large extent, and it is felt that the values obtained represent the heat of formation of these addition compounds. It will be noted that the standard deviations in the enthalpies are, in general, larger for the aliphatic amines because of this decomposition.

Discussion

The measured value of the equilibrium constant, K, serves to determine the standard free energy change, $\Delta G°$. The ΔH reported here is not actually $\Delta H°$ unless we assume that all heats of dilution are negligible. The concentration of VO(acac)$_2$ was kept so low (0.02 M) that no detectable ΔH_{dil} could be measured, and the same was true of the adducts. In the case of the bases, ΔH_{dil} was measured as a function of concentration for piperidine and methanol, as shown in

parent in the first column of data in Table III. The inductive effect of enhancement of the base strength of pyridine by substitution of methyl groups is well

Table IV. Heat of Adduct Formation toward Vanadyl Trifluoroacetylacetonate in Nitrobenzene at 25°

Ligand	$-\Delta H°$, kcal./mole
Pyridine	8.80 ± 0.14
3-Picoline	8.49 ± 0.21
4-Picoline	10.17 ± 0.19
3,5-Lutidine	7.53 ± 0.42
3,4-Lutidine	8.16 ± 0.14

illustrated by the enthalpy change of the picolines compared to that of pyridine. The steric effect of bulky groups near the coordination site of the amine may be observed by comparing the $\Delta H°$ values for piperidine (− 10.06 kcal./mole) and 2-methylpiperidine (−7.69 kcal./mole), for example, as well as n-butylamine (− 10.42 kcal./mole) and di-n-butylamine (−9.33 kcal./mole).

On the other hand, a consideration of inductive ef-

fects would also lead one to expect the lutidines to coordinate to vanadyl acetylacetonate with a heat more negative than either pyridine or the picolines,

Table V. Heat of Dilution of Bases in Nitrobenzene

Base	Dilution range, M	Approx. ΔH, cal./mole
Piperidine	0.4–0.2	−24
	2.0–1.0	36
Methanol	5.0–2.5	404
	1.0–0.5	444

and sterically hindered 2,6-lutidine to have a heat much less negative than the other pyridines. However, these are not the experimental results. This leads us to the measure of relative base strength favored by Bell, among others.[12] This scale is the equilibrium constant or, equivalently, the free energy change for the reaction. One important reason for using this scale is that variations in the free energy of solvation are usually smaller than variations in the enthalpy of solvation. A well-known example concerns the ionization of substituted carboxylic acids, where $\Delta G°$ follows a sensible progression, while $\Delta H°$ is erratic.[12] Now using $\Delta G°$ as the measure of base strength, the 3,5- and 3,4-lutidines fall into line. Furthermore, the free energy changes for the five pyridines (excluding sterically hindered 2,6-lutidine) vary linearly with pK_a[13] and the Hammett σ-values of these bases. The 2,6-lutidine is now found to be a weaker base than pyridine, as would be predicted from steric considerations.

Several comments concerning the entropy changes can safely be made within the accuracy of the determination of $\Delta S°$. The most negative entropy changes reported, those governing the adduct formation by diethylamine and di-n-butylamine, are consistent with the large loss of rotational entropy which these ligands must suffer upon coordination. Similarly, as has been mentioned above, $\Delta G°$ is a better measure of the base strength of 2,6-lutidine in this system than is $\Delta H°$. This means that the steric effect caused by the α-methyl groups is best viewed as an entropy effect, rather than an enthalpy effect.

It should be noted that the acid $VO(acac)_2$ is a somewhat less sensitive indicator of relative base strengths than is the proton. The ligands listed in Table III span a range in pK_a from about −3 for methanol[14] to 11.27 for pyrrolidine.[15] The $\Delta H°$ values for the acid $VO(acac)_2$ range from −5.77 kcal./mole to −10.47 kcal./mole for methanol and pyrrolidine, respectively; the equilibrium constants toward $VO(acac)_2$ for these two ligands are separated only by a factor of about 2 × 10³.

The amine function of morpholine appears to be the basic center, for not only does the heat of its reaction with $VO(acac)_2$ approximate that of other secondary

(12) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.
(13) R. J. L. Andon, J. D. Cox, and E. F. G. Herington, *Trans. Faraday Soc.*, **50**, 918 (1954).
(14) H. E. Wirth and P. I. Slick, *J. Phys. Chem.*, **66**, 2277 (1962); E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 4999 (1960).
(15) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 140, 141.
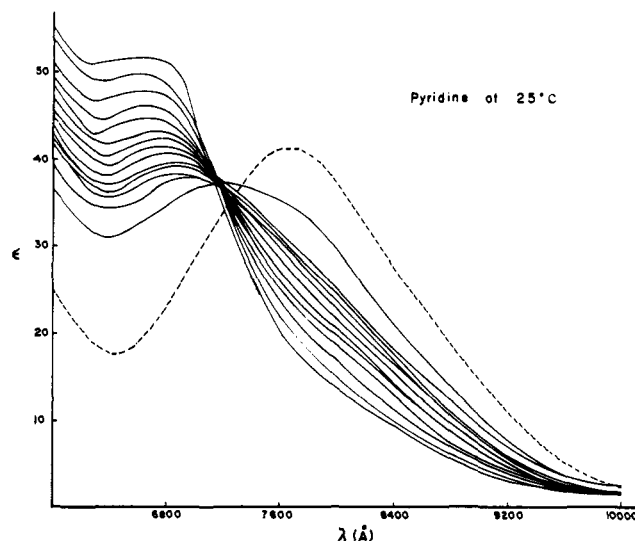
Figure 1. Spectrum of vanadyl acetylacetonate in benzene as increments of pyridine are added. The thirteen inner lines are for pyridine concentrations of 0.002 to 0.04 M. The dotted line illustrates the spectrum in pyridine as solvent; there is about a factor of 300 increase in base concentration on going from the most concentrated solution of pyridine in benzene to pure pyridine.

amines, but also dioxane has been found to react only very weakly with vanadyl acetylacetonate. Other bases which have been found to affect the spectrum of $VO(acac)_2$ to an extent too small for us to measure the equilibrium constants include thiourea, acetone, acetonitrile, triphenylphosphine, and the constrained phosphite, $P(OCH_2CH_2)_3CCH_3$.[16] These observations agree with the known weak electron-donating abilities of these compounds (*i.e.*, $VO(acac)_2$ cannot form π-bonds to the base).

Since methanol has been found to function both as a base and as a hydrogen-bonding ligand, as described below, the equilibrium constant given in Table III is an upper limit on the actual value. ΔH is probably also a composite of adduct formation and hydrogen-bond formation.

In comparing the $\Delta H°$ values for the $VO(acac)_2$–B system (Table III) with those for the $VO(TFACA)_2$–B system (Table IV), where B is a substituted pyridine, we find in every case that the trifluoro derivative gives a more negative $\Delta H°$. Qualitatively, it is reasonable for the $\Delta H°$ values to be more negative for $VO(TFACA)_2$, for the electron-withdrawing effect of the trifluoromethyl group should make the vanadium a more positive dipole, thus attracting the amine more strongly. It would be interesting to see if ΔG is again a linear function of pK_a. Unfortunately the change in the visible spectrum is not large enough to allow determination of the equilibrium constants.

Another observation which we believe to be significant follows. The postulate[1-3] that the spectral shift upon coordination to $VO(acac)_2$ is due to the perturbation in the sixth position suggests that the magnitude of the spectral shift should be directly related to the strength of the interaction. We find this not to be true. Methanol and hexamethylphosphoramide, OP-$(NMe_2)_3$, cause the largest spectral shifts that we have observed, but have the smallest heats of reaction

(16) A kind gift from Professor J. G. Verkade, Iowa State University, Ames, Iowa.

for the coordination reaction. Since the energy level scheme[4] for the vanadyl ion appears to be well substantiated, at least for the lowest energy levels,[3] an explanation of this anomaly is not apparent. Some of the results may, however, be explained by hydrogen bonding, as the following experiments suggest. A solution of $VO(acac)_2 \cdot$ pyridine $+ 5 M$ methanol in nitrobenzene absorbs at 12,930 cm.$^{-1}$ (ϵ 37.0), which is a greater shift from the band for $VO(acac)_2$ than is that for $VO(acac)_2 \cdot$ pyridine; since the equilibrium constants show that the methanol cannot displace the pyridine from its adduct, the most likely explanation for the enhanced spectral shift is hydrogen bonding, presumably to the vanadyl oxygen. Furthermore, $VO(acac)_2$ is not very soluble in water, which is certainly a weaker base than most of the ligands considered here, yet a concentrated enough solution of $VO(acac)_2$ in water can be obtained for spectral purposes. We find the first band shifted in this case to 12,240 cm.$^{-1}$ (ϵ 39.4), which is by far the largest shift that has been observed in this system. Since hydrogen bonding is so prevalent in this solvent, a substantial part of the spectral shift must be due to this interaction.[17] This does not resolve the whole question, for triphenylphosphine oxide and hexamethylphosphoramide, neither of which is capable of hydrogen bonding in the manner of methanol and water, also cause large spectral shifts. Experiments now underway on the electron spin resonance spectra of these adducts may help to resolve the question.

One would like to find some correlation between the spectral data and the nature of the ligand, but we have been unable to find any useful correlation. Thus, the frequency of the first band, ν_1 (Table I), is remarkably constant for almost all the amines, and therefore there is little correlation with any of the thermodynamic functions. This band occurs at slightly lower energy for the oxygen donors, and we have commented above on this fact. The extinction coefficient, ϵ_1, is slightly lower for aliphatic amines than for the aromatic amines. The energy, ν_2, of the second band is approximately constant throughout the series of donors, but the aromatic amines appear to cause a small shift to higher energy. Note also that, for oxygen donors, ϵ_2 is significantly smaller (Table I; also, $\epsilon_2 = 9$ for water) than for the amine donors.

Substitution of acetylacetonate ligand by trifluoroacetylacetonate causes a red shift in ν_1, but hardly any shift in ν_2 results. This is difficult to reconcile with the molecular orbital calculations[3,4] on vanadyl ion, for ν_1 is supposed to consist of a transition from a pure metal d-orbital in the VO_4 plane to an excited state in which the only ligand orbitals involved are the π-orbitals on the vanadyl oxygen and should not depend on the in-plane ligand field. The second excited state contains σ-bonding due to the acetylacetonate ligands, and we anticipated that its energy would be sensitive to fluorine substitution. These results imply that the molecular orbitals for the vanadyl ion are more complex than had been supposed heretofore.

It is also interesting that the shift of ν_1 for VO-$(TFACA)_2$ on coordination to pyridine is less than half that found in the parent acetylacetonate system.

A possible explanation suggests that the trifluoroacetylacetonate ligand causes a decrease in the electron density on the vanadium, which in turn allows an increase in the strength of the $V{=}O$ bond. This would shift ν_1 to lower energies and cause the perturbation due to addition of pyridine to have a smaller effect on ν_1 than is found in $VO(acac)_2$. On the other hand, this is a second-order effect which might not be important.

In comparing the above results to other studies of Lewis acid–base reactions, we find a qualitative correlation with the $B(CH_3)_3$–amine studies reported by Brown and co-workers[18a] in the order of base strengths, and a semiquantitative agreement with the calorimetric results for the reaction of pyridine and the 3- and 4-picolines with copper acetylacetonate.[18b] For example, the enthalpy change of -6.05 ± 1.03 kcal./mole for the reaction of pyridine with $Cu(acac)_2$ in benzene may be compared with our value of -7.35 ± 0.19 kcal./ mole (nitrobenzene). While the heat of the reaction of quinoline with $Cu(acac)_2$ has not been reported, the equilibrium constant (methylene chloride, 30°)[19] of 1.5 ± 0.1 l./mole may be compared with the value of 1.86 ± 0.23 l./mole reported here for the vanadyl reaction. Although a statistical factor of two enters into the latter example, these results imply that the doubly bonded oxygen close to the vanadium atom does not appreciably affect the acceptor properties of a metal in an $M(acac)_2$ ring system.

The results of this research also invite comparison with those of Sacconi and co-workers[20–23] on diacetyl-bis(benzoylhydrazino)nickel(II), NiDBH, as a reference acid. This is made difficult by the fact that NiDBH always accepts two molecules of base, and the stepwise thermodynamic functions have not been evaluated; another factor which is not easily gauged is that Ni-DBH changes spin state upon addition of 2 moles of base, while, of course, there is no such change with $VO(acac)_2$. Nevertheless, several interesting facets emerge. Steric strain appears to be comparable with the two reference acceptors, as evidenced by a comparison of the relative affinities of, say, pyridine and 2,6-lutidine; again, steric effects tend to appear in ΔS, rather than ΔH. Pyridine and the picolines appear to follow parallel trends in their relative donor abilities. The change in equilibrium constant, K, for quinoline is parallel between the two systems, but the enthalpy change is not.

An earlier examination[24] of vanadyl acetylacetonate addition compounds dealt with the equilibrium vapor pressure over the solid adducts, but the thermodynamic quantities reported are difficult to relate to those characteristic of the formation of the coordinate bond.[25,26]

(17) See also J. Selbin and T. R. Ortolano, *J. Inorg. Nucl. Chem.*, **26**, 37 (1964).

(18) (a) E. A. Braude and F. C. Nachod, Ed., "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, N. Y., 1955, pp. 639, 640; (b) W. R. May and M. M. Jones, *J. Inorg. Nucl. Chem.*, **25**, 507 (1963).

(19) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 5399 (1963).

(20) L. Sacconi, G. Lombardo, and P. Paoletti, *ibid.*, 848 (1958).

(21) L. Sacconi, G. Lombardo, and R. Ciofalo, *J. Am. Chem. Soc.*, **82**, 4182 (1960).

(22) L. Sacconi, G. Lombardo, and P. Paoletti, *ibid.*, **82**, 4185 (1960).

(23) L. Sacconi and G. Lombardo, *ibid.*, **82**, 6266 (1960).

(24) R. T. Claunch, T. W. Martin, and M. M. Jones, *ibid.*, **83**, 1073 (1961).

(25) For a discussion of the difficulties inherent in studying coordination equilibria in the solid state due to the uncertainties in crystal lattice energies, see R. W. Parry and R. N. Keller, "The Chemistry of the Co-

ordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, pp. 137–143.
(26) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

Arylazoplatinum Compounds

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Several arylazoplatinum compounds, Ar–N=N–PtCl-[P(C_2H_5)$_3$]$_2$, have been prepared by the reaction of arenediazonium salts with HPtCl[P(C_2H_5)$_3$]$_2$. The azo compounds are stable, highly colored solids which may be decomposed catalytically to give the corresponding arylplatinum compounds, trans-ArPtCl[P(C_2H_5)$_3$]$_2$. Spectral studies of these complexes indicate substantial interaction of the platinum d-orbitals with the azo π-orbitals.

The reaction of diazonium salts with metal halides has been used extensively for the preparation of arylmetal compounds.[1] Arylazometal complexes were postulated as intermediates in this reaction but no such compounds were isolated until recently when King and Bisnette[2] described *p*-anisylazo-π-cyclopentadienyldicarbonylmolybdenum. It has been suggested that a Co–N bond exists in cobalt chloride complexes of benzenediazonium chlorides.[3] However, more recent spectroscopic studies[4] indicate that the spectral shifts ascribed to Co–N bonding were actually due to charge-transfer phenomena.

Arylazoplatinum compounds in which an arylazo function is σ-bonded to platinum have now been prepared.

Synthesis. Benzenediazonium tetrafluoroborate reacts with *trans*-chlorohydridobis(triethylphosphine)-platinum[5] (**1**) to give a yellow crystalline salt which probably has structure **2**. Treatment of this salt with methanolic KOH gives red crystals of *trans*-chloro-(phenylazo)bis(triethylphosphine)platinum (**3**). Products corresponding to **3** have also been obtained by reaction of *m*-fluoro-, *p*-fluoro-, and *p*-nitrobenzenediazonium salts with the hydride (**1**). Reaction of *p*-methoxybenzenediazonium tetrafluoroborate with **1**

gave only the *p*-methoxyphenylplatinum compound analogous to **4**.
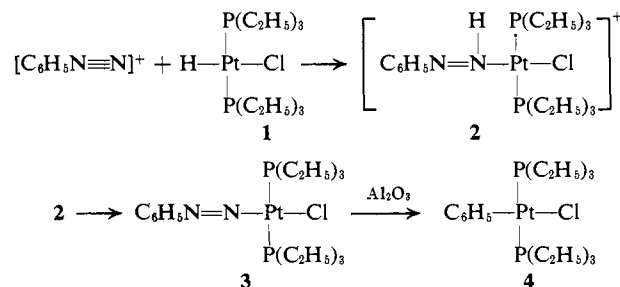
The initial step in the reaction sequence is probably addition of the diazonium salt to the square-planar platinum complex followed by migration of a hydrogen from the platinum to the adjacent nitrogen atom to give **2**. A similar proton transfer has been observed in the reaction of diazonium salts with the $B_{10}H_{10}^{-2}$ ion.[6] The proton n.m.r. spectra of **2** and the analogous *m*- and *p*-fluorophenyl complex salts in CDCl$_3$ show peaks at *ca.* τ −5[7] assignable to the NH proton. The phenyl salt (**2**) gives a fairly sharp peak. On dilution with trifluoroacetic acid, proton exchange occurs, and the peak is broadened and shifted to higher field.

The neutral azo complexes (**3**) are red or green crystalline solids which melt to give highly colored liquids. The melts decompose with evolution of nitrogen at *ca.* 120°. Solutions in hydrocarbon solvents appear to be stable for several days. Solutions in CCl$_4$ or CHCl$_3$ rapidly decolorize with evolution of nitrogen.

Attempts to chromatograph the neutral compounds on active neutral alumina gave only *trans*-arylchlorobis-(triethylphosphine)platinum derivatives such as **4**. Although several of these compounds have been prepared by Grignard reactions,[8] the catalytic decomposition of the arylazo complexes is probably an equally convenient route to the *trans* series. This route is particularly valuable for synthesis of compounds such

(1) A. N. Nesmeyanov, "Selected Works in Organic Chemistry," translated by A. Birron and Z. S. Cole, The Macmillan Co., New York, N. Y., 1963, presents numerous examples of this technique.
(2) R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 5694 (1964).
(3) L. A. Kazitsina, O. A. Reutov, and Z. F. Buchovskii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1523 (1960).
(4) (a) E. A. Boudreaux, H. B. Jonassen, and L. J. Theriot, *J. Am. Chem. Soc.*, **85**, 2039, 2896 (1963); (b) R. H. Nuttall, E. R. Roberts, and D. W. A. Sharp, *Spectrochim. Acta*, 17, 947 (1961).
(5) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(6) M. F. Hawthorne and F. P. Olsen, *J. Am. Chem. Soc.*, **86**, 4219 (1964).
(7) τ = 10 − Δ(Me$_4$Si)/oscillator frequency: G. V. D. Tiers, *J. Phys. Chem.*, **62**, 115 (1958).
(8) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).