in 12 hours. This number is about one millionth the number of all the molecules present and of course an even smaller fraction of the number of molecules reacting in 12 hours. One may infer that the radiation from a few microcuries of I^{131} will have a negligible effect in shifting the diiodoethane equilibrium. Viewed differently, the calculation above shows also that the Xe^{131} resulting from the I^{131} decay never contributes appreciably to the pressure of the system nor do possible products of radiation-induced decomposition of ethylene. A direct comparison of the data in Table I with the results of earlier investigators, therefore, seems proper.

One may check the $\Delta H°$ values obtained from equilibrium studies with those derived from thermochemical data. Depending on which data form the basis of the calculations, $\Delta H°$'s ranging from 11.6 to 20.4 kcal./mole may be calculated. The lower figure is obtained if one chooses what seem to be the best available data for (1) the heat of combustion of solid 1,2-diiodoethane (only one value is available, namely, 324.8 kcal./mole reported by Berthelot),[16] (2) the heat of sublimation of iodine (Giauque's figure[17] of 14.88 kcal./mole was chosen), (3) the heat of sublimation of diiodoethane (the only published value is Mooney and Ludlam's,[1] namely, 15.7 kcal./mole) and (4) the heat of combustion of ethylene (the best among the rather discrepant values seems to be the Bureau of Standards' result,[18] *viz*, 337.2 kcal./mole). The agreement between the $\Delta H°$ based on the best available thermochemical data and the $\Delta H°$ found in the present equilibrium study seems better than would have been expected.

The equilibrium constant at 25° computed from equation 1 is equivalent to a $\Delta F°$ value at 25° of 2.1 kcal./mole. By combining this result with $\Delta H°$ in the usual way, *viz.*, through the relation

$$\Delta F° = \Delta H° - T\,\Delta S°$$

one estimates for $\Delta S°$ a magnitude of 31.2 cal./deg./mole. $\Delta S°$ is the difference between the entropy of a mole of gaseous 1,2-diiodoethane and the sum of the entropies of a mole of iodine and a mole of ethylene all at 25° and 1 atm. The latter two molal entropies are 62.29 for iodine[19] and 52.45 for ethylene.[20] Using these entropy values, we find the entropy of a mole of 1,2-diiodoethane to be 83.2 cal./deg. This figure conforms well to the entropies estimated for the corresponding chlorine and bromine compounds[21] as shown in Table II. The figure 83.2 entropy units agrees well also with the molal entropy value of 83 cal./deg. computed statistically.[22]

TABLE II

STANDARD MOLAL ENTROPIES OF DIHALOETHANES AT 25°, CAL./DEG.

1,2-Dichloroethane[21]	73.9
1,2-Dibromethane	78.8
1,2-Diiodoethane[a]	83.2
1,2-Diiodoethane[b]	77.3

[a] Present work. [b] From an equation for K_p derived by Cuthbertson and Kistiakowsky from a combination of their own data with the data of Mooney and Ludlam.

Acknowledgment.—The authors are grateful to Dr. Richard M. Noyes for help in the design of the G. M. counting tube.

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[16] M. Berthelot, *Ann. chim. phys.*, **21** [7], 296 (1900). The figure quoted has been adjusted to the modern molecular weight of diiodoethane.

[17] W. F. Giauque, THIS JOURNAL, **53**, 507 (1931).

[18] E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 269 (1946).

[19] G. M. Murphy, *J. Chem. Phys.*, **4**, 434 (1936).

[20] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffee, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952, p. 120.

[21] W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.*, **16**, 303 (1948).

[22] A. Abrams and T. W. Davis, forthcoming publication.

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Some Vanadyl Complexes with β-Diketones

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The preparation and properties of a number of complexes between the vanadyl ion and β-diketones are described. These substances are shown to fall into two groups, one of which apparently shows five coördinated vanadium(IV), and one of which shows six coördinated vanadium(IV). The reactions of the five coördinated compounds with bases to give compounds in which the central vanadium has a coördination number of six are dependent upon both the strength of the base and the presence of favorable stereochemical factors.

Although vanadyl complexes with acetylacetone and benzoylacetone have been known for several decades,[1,2] there have been no detailed descriptions of their reactions nor information on the type of diketone which may be used to form such complexes. The purpose of the present work is to provide information on both of these subjects. Several complexes have been prepared and their substitution reactions studied.

The common methods of preparing vanadyl acetylacetonate yield a turquoise blue solid which has been formulated as $VO(C_5H_7O_2)_2$[1] or $VO(C_5H_7O_2)_2 \cdot H_2O$.[2] The analysis of the product as well as its physical properties[3] support the former composition and would lead to the conclusion that this substance is either polymeric or an example of five coordinated vanadium(IV). The few reactions of this compound which have been studied were formulated by Rosenheim as replacement

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[1] G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, **103**, 78 (1914).

[2] A. Rosenheim and Hsing Yu Mong, *Z. anorg. Chem.*, **148** 34 (1925).

[3] B. P. Block (in a personal communication to Prof. T. Moeller) reports that the properties of vanadyl bis-(acetylacetonate) prepared as reported in this paper are identical with those of the acetylacetonate of vanadium prepared under completely anhydrous conditions.

reactions in which the coördinated water is removed and another ligand takes its place[2]

$$\mathrm{VO(acac)_2 \cdot H_2O + B \longrightarrow VO(acac)_2 \cdot B + H_2O} \quad (1)$$

Here B represents some base (such as ammonia or pyridine) and acac represents the ion $[\mathrm{CH_3COCHCOCH_3}]^-$. If, however, this compound is $\mathrm{VO(acac)_2}$ or a polymer the reaction is merely one of addition

$$\mathrm{VO(acac)_2 + B \longrightarrow VO(acac)_2 \cdot B} \quad (2)$$

$$\text{or } \mathrm{[VO(acac)_2]_x + xB \longrightarrow xVO(acac)_2 \cdot B} \quad (3)$$

In reaction 2 we would have coördinated vanadium which can take up another ligand if the ligand is a strong enough base. On this basis the reaction of vanadyl bis-(acetylacetonate) and ammonia might follow one of two possible courses.

If the complex has an octohedral configuration with an empty orbital the ligand merely adds to the complex in this position, no stereochemical rearrangement being required. An alternate picture, suggested by the referee, gives the complex a trigonal bipyramidal structure. In this case the reactions would involve a minor rearrangement of the groupings already present in the complex when addition of a ligand occurred. This structure is fully capable of explaining the reactions studied. In either case the addition reaction is of interest because it apparently involves the increase of the coördination number of the central vanadium atom from five to six, both compounds being stable. Although the customary picture of complex formation is one in which ligands coördinate stepwise, examples of stable compounds in which the maximum coördination number is not achieved are quite rare.

If the compound is a polymer, however, this problem does not arise, the sixth coördination position being involved in polymerization. The oxygen atom in the vanadyl ion is formally capable of filling positions in the coördination spheres of two vanadium atoms. With this type of compound the reaction with another ligand would involve depolymerization. The reaction would then merely replace one of the oxygen atoms of each vanadium atom with another ligand.

The experimental work presented falls naturally into two sections, the preparation and chemical reactions of vanadyl diketone complexes, and a study of the physical properties of these compounds.

Experimental

The vanadyl sulfate used in the preparation of the complexes was either $\mathrm{VOSO_4 \cdot 2H_2O}$, C.P. from the Fisher Scientific Co., or $\mathrm{VOSO_4}$, C.P. from the Vanadium Corporation of America. Aqueous solutions of these compounds were prepared using dilute sulfuric acid (10% by volume), a step made necessary by the hydrolysis of the vanadyl sulfate in water.[4]

Vanadyl Bis-(acetylacetonate).—This was prepared by the method of Rosenheim and Mong.[2] This substance does not melt but decomposes at temperatures above 200°. This compound was used in the preparation of substituted vanadyl bis-(acetylacetonates) described below. *Anal.* Calcd. for $\mathrm{VC_{10}H_{14}O_5}$: C, 45.3; H, 5.28; V, 19.3. Found: C, 45.6; H, 5.45; V, 19.2.

Vanadyl complexes with other β-diketones were prepared by a similar method. Because of the slight solubility of the diketones in water, they were first dissolved in ethanol and then added to the solution of vanadyl sulfate in dilute sulfuric acid. Neutralization was effected by a 10% solution of sodium carbonate as before. These substances generally settled out of solution as oils which subsequently solidified. The properties of these compounds are presented in Table I.

TABLE I

VANADYL COMPLEXES WITH β DIKETONES

Diketone	Color of complex	Analyses, % Calcd. C	H	V	Found C	H	V
2-Thenoyltrifluoroacetone[a]	Olive drab	36.3	1.9	9.6	34.4	2.6	9.2
2-Thenoylperfluorobutyrylacetone	Light green	32.6	1.2	6.3	34.9	1.4	5.6
2-Furoyltrifluoroacetone	Light green	38.8	2.0	10.3	38.8	2.6	10.3
2-Furoylperfluorobutyrylacetone	Brownish green	33.2	1.3	6.4	34.6	1.6	6.8
Benzoylacetone	Dark green	62.0	4.6	13.1	60.8	4.6	12.9

[a] Considerable difficulty was encountered in obtaining a sample of this compound which could be analyzed before extensive decomposition.

Substituted Vanadyl Bis-(acetylacetonates).—The method used to prepare these compounds was varied according to the solubility of the resultant complex in ether. When the complex formed was appreciably soluble in ether the reactants were refluxed in ether and then the reaction mixture was filtered. The ether solution was then evaporated and the solid complex obtained. This method is designated as procedure "A." When the resulting complex was relatively insoluble in ether, the procedure used by Rosenheim and Mong[2] for the preparation of the pyridine complex with vanadyl bis-(acetylacetonate) was used. Here the vanadyl bis-(acetylacetonate) was refluxed in ether with an amount of ligand in excess of that required and the solid residue is found to be the complex desired. This method is restricted to ligands which are volatile liquids or solids readily soluble in ether. It is designated as procedure "B." Table II contains a summary of the properties of these compounds.

Other Ligands Studied.—A number of other ligands were used without effecting any reaction. Among these were acridine, triphenylarsine, methanol, ethanol, hydrogen sulfide, triethylamine, 2,5-dimethylpyridine, and triphenylphosphine. With hydrazine a vigorous reaction accompanied by the evolution of gas and the deposition of a brown solid resulted, a reduction to trivalent vanadium and the formation of a hydrazide being probable. Several of the complexes with aliphatic amines were prepared but found to be unstable, undergoing decomposition at room temperature.

Substituted Vanadyl Bis-(benzoylacetonates).—These were prepared using the methods outlined in the section on substituted vanadyl bis-(acetylacetonates). Table III lists these compounds and their properties.

Molecular Weight Determinations.—The molecular weights of both vanadyl bis-(acetylacetonate) and vanadyl bis-(benzoylacetonate) were determined ebullioscopically in benzene. The solubility of these substances in benzene at its freezing point was found to be too small to allow a ready determination of the molecular weight cryoscopically. The apparatus used for the boiling point determinations was a modified Cottrell apparatus fitted with a Beckmann thermometer and a Glasco electrical heating mantle. The average of several measurements on vanadyl bis-acetylacetonate gave this substance a molecular weight of 252 ± 10 in benzene, for the vanadyl bis-(benzoylacetonate) the molecular weight was found to be 395 ± 10°.

Discussion

The observed reactions and the analyses of the products obtained are not all consistent with the assignment of a coördination number of six to the V^{+4} ion. The alternate interpretations which are most obvious are the presence of five coordinated vanadium in some of these complexes or polymeric structures in which vanadium achieves a coördination number of six by the sharing of the vanadyl oxygen atom.

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(4) L. Meites, THIS JOURNAL, **75**, 6059 (1953).

TABLE II

SUBSTITUTED VANADYL BIS-(ACETYLACETONATES)

Ligand	Method of prep.	Color	Analyses, % Calcd. C	H	N	V	Found C	H	N	V
Isoquinoline	B	Gray-green	57.7	5.57	3.54	12.9	57.9	5.66	3.60	12.9
Piperidine	A	Light green	51.6	6.87	4.01	14.6	48.2	6.85	3.91	14.4
γ-Picoline	B	Light green	53.6	5.87	3.91	14.2	51.1	5.54	4.03	14.1
Methylamine	A	Dark green	44.6	6.42	4.72	17.2	45.0	6.67	4.51	16.9

TABLE III

SUBSTITUTED VANADYL BIS-(BENZOYLACETONATES)

Ligand	Method of prep.	Color	Analyses, % Calcd. C	H	N	V	Found C	H	N	V
Pyridine	A	Brown	64.0	4.92	2.99	10.9	64.35	5.03	2.79	10.3
Methylamine[a]	B	Brown	60.0	5.48	3.32	12.1	57.8	5.90	3.38	11.9
Isoquinoline	B	Brown	67.5	4.83	2.70	9.85	67.0	5.01	2.75	10.1
γ-Picoline	B	Brown	64.7	5.19	2.91	10.6	63.0	5.07	2.76	10.7

[a] This complex was found to be very unstable. The original brown solid turned green on standing. The decomposition product was analyzed with the following results, V 14.2%, C 59.8%, H 4.83%, N 0.32%. The decomposition appears to involve a more profound change than the evolution of methylamine.

A decision between these views may be made on the basis of molecular weight determinations in an inert solvent. Although Morgan and Moss determined the molecular weight of vanadyl bis-(acetylacetonate) they used chloroform as a solvent. Subsequently Pfeiffer and his co-workers[5] showed that chloroform is capable of reacting with certain vanadyl complexes to form adducts stable at room temperature. The use of benzene avoids this type of reaction. Both compounds studied were found to be present as monomers in benzene solution. The molecular weights of monomeric vanadyl bis-(acetylacetone) and vanadyl bis-(benzoylacetone) are 259 and 389, respectively, and the experimental values found were 252 and 395, respectively. This together with the results of the chemical analyses of the vanadyl bis-(acetylacetonate) lead to the formula $VO(C_5H_7O_2)_2$. This is in agreement with the work of Morgan and Moss[1] though not that of Rosenheim and Mong.[2] A comparison of the published analyses of this compound, together with the analyses listed above is given in Table IV.

TABLE IV

PUBLISHED ANALYSES OF VANADYL BIS-(ACETYLACETONATE)

	C, %	H, %	V, %
Rosenheim and Mong	41.5	..	18.32 17.58
Morgan and Moss	45.1	5.7	18.65
This paper	45.6	5.45	19.2
Theor. for $VO(C_5H_7O_2)_2$	45.3	5.28	19.2
Theor. for $VO(C_5H_7O_2)_2 \cdot H_2O$	42.4	5.65	18.1

A further test for the presence of coördinated water was made using the infrared absorption spectra of this and related substances. Complex compounds containing coördinated water show absorption bands in the region 3200–3600 cm.$^{-1}$ (*e.g.*, $[Co(NH_3)_5(H_2O)]Br_3$ shows a band at 3270 cm.$^{-1}$ due to coördinated water). Of the vanadyl compounds prepared, the compounds with the following diketones showed no absorption bands in this region: acetylacetone, benzoylacetone, 2-thenoylperfluorobutyrylacetone, and dibenzoylmethane. The compounds with the following diketones showed absorption bands in the region indicated: 2-furoylperfluorobutyrylacetone (3570 cm.$^{-1}$), and 2-furoyltrifluoroacetone (3530 cm.$^{-1}$). These data confirm the formulation of the benzoylacetonate and the acetylacetonate offered by Morgan and Moss.

The substitution reactions studied are of interest as they show clearly two of the factors involved in determining whether or not a reaction will occur. The first of these factors is the base strength of the ligand. In the reactions studied neither oxygen in –O– structures nor sulfur in –S– structures is capable of coördinating. These are weaker bases than nitrogen in ammonia and substituted ammonias. A second factor is steric in nature. The nitrogens in quinoline, isoquinoline and acridine are about equally basic, yet acridine, in which the nitrogen is shielded on both sides, by aromatic systems, does not complex. Quinoline, in which the nitrogen is shielded on one side, and isoquinoline, in which the nitrogen is not shielded, both form complexes readily. This steric factor is also present in the compounds triethylamine and 2,5-dimethylpyridine, neither of which complex. It is probable that both the weakness of the central atom as a base and the steric factor are operative in the case of triphenylarsine and triphenyl phosphine, which are also unreactive.

The fact that quinoline reacts readily, whereas acridine does not react at all would favor a structure for vanadyl acetylacetonate in which the grouping of ligands about the "empty" orbital is not symmetrical, *i.e.*, a *cis*-configuration for the oxygen and the orbital. If this is true this compound should be resolvable into enantiomorphs.

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(5) P. Pfeiffer, *et al.*, *J. prakt. Chem. N. F.*, **149**, 217 (1937).