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Thermodynamics of Coördination to an Unsolvated Position in Oxovanadium(IV) Chelates

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Vapor pressure measurements have been used to obtain enthalpies, entropies and free energies of coördination to the sixth, unsolvated position in bis-(2,4-pentanediono)-oxovanadium(IV). The coördination of ammonia, methylamine, ethylamine, isopropylamine or tertiary butylamine, each referred to the standard state at unit atmosphere, is found to be accompanied by enthalpy changes of the order of 15 kcal./mole, but the corresponding free energy changes are relatively small. The entropy changes are such that the coördination process may be assumed to result in the complete loss of the translational entropy of the ligand together with a partial loss of some of its rotational entropy. The entropy changes attributable to changes in the solid phase are quite small. The total entropy changes found are of the order of 40 e.u. and are considerably larger than those normally reported for comparable processes in solution. It seems reasonable to believe that the values are more nearly characteristic of the changes to be found in a reaction in which mere coördination occurs rather than the values derived from the study of competitive solvation processes in solution. There seems to be little correlation of the results with specific chemical properties of the ligands, although the ΔF^0 values for substituted amines are inversely related to their pK_a values. Coördinate bond energies for the ligands studied varied from 15 to 17 kcal./mole. The similarities of the process observed to a phase change in a two component system are emphasized as well as the importance of the data obtained in such systems for a knowledge of the coördination act involving a bare coördination site rather than a competitive reaction in solution.

By far the greatest portion of the information available on the thermodynamics of coördination is derived from competitive processes involving the rivalry of solvent and ligand for a coördination site. One good reason for this is that there are relatively few well defined opportunities for studying coördination to a bare coördination site on a metal. Certainly, there is a wealth of information available on systems involving the boron halides and related boron compounds.[3] The number of such studies involving transition element coördination compounds, however, is very small.

The chief requirement which must be met before these systems can furnish unambiguous information on coördination is that no additional processes occur in addition to coördination. Since by far the largest number of transition metal-complexes studied by vapor pressure measurements undergo additional processes such as a change of charge type or a change in the crystal lattice structure, they obviously are not capable of furnishing straightforward information on the coördination process *per se*. Thus suitable systems for such a study are restricted to those cases where, at most, only slight additional changes accompany the change in coördination number. All of these are systems where coördination involves two or more accessible coördination numbers, preferably with stereochemical arrangements which are related to each other by the successive addition of ligands to previously empty positions of the coördination sphere. Such are the transitions from a square planar to an octahedral configuration as found for Ni(II),[4] Pd(II)[5] and Pt(II)[6] or the change from a tetragonal pyramid to an octahedral configuration such as is

found for many VO^{2+} chelates.[7–9] The study of some examples of this second sort is presented in this paper. These were selected because it was felt that there would be less ambiguity in the interpretation of the data and because such a choice would allow a ready comparison of the results with the large amount of data available on the change from a planar trigonal to a tetrahedral configuration in the compounds of boron. An additional advantage is that data on such a simple process should allow a comparison to be made of theoretical calculations of energies of coördination.

The systems examined consisted of a non-volatile chelate, bis-(2,4-pentanediono)-oxovanadium(IV), and a volatile amine which reacted to give a complex in which the sixth coördination position is occupied by the amine nitrogen, *e.g.*, for the NH_3 system

$$VO(C_5H_7O_2)_2NH_3 \rightleftarrows VO(C_5H_7O_2)_2 + NH_3$$

The stereochemical course of this reaction is depicted in Fig. 1. Since these complexes possess a readily measurable dissociation pressure, this property was determined at several temperatures. The thermodynamic changes involved then were calculated using the equations

$$\Delta F^0 = -RT \ln K_P = -RT \ln P_{amine}$$

$$\Delta H = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{P_2}{P_1}$$

$$\Delta F^0 = \Delta H^0 - T\Delta S^0$$

Experimental

Preparation of the Complexes.—The bis-(2,4-pentanediono)-oxovanadium(IV) was prepared using the method given in "Inorganic Syntheses."[10] The product then was analyzed with the results, calcd. for $VC_{10}H_{14}O_5$: V, 19.25%; C, 45.28%; H, 5.28%. Found: V, 19.25%; C, 44.77%; H, 5.08%. The amine adducts were prepared by two methods. In the first method, used for amines which are gaseous at room temperature, a stream of the amine vapor (previously dried by passage through a column, twenty eight

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(3) Much of the work on these systems up to 1954 has been collected by H. C. Brown, D. M. McDaniel and O. Hafliger in "Determination of Organic Structures by Physical Methods," ed. by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955, ch. 14.

(4) J. B. Wills and D. P. Mellor, THIS JOURNAL, 69, 1237 (1947); S. Shibata, *Bull. Chem. Soc. Japan*, 30, 842 (1957).

(5) A. Rosenheim and T. A. Mass, *Z. anorg. Chem.*, 18, 331 (1898).

(6) L. Tschugaeff and W. Lebedinski, *Compt. rend.*, 161, 563 (1928); L. F. Heneghan and J. C. Bailar, Jr., THIS JOURNAL, 75, 1840 (1953).

(7) M. M. Jones, THIS JOURNAL, 76, 5995 (1954); M. M. Jones, *Z. Naturforschung*, 12b, 595 (1957).

(8) R. P. Dodge, U.C.R.L. Report 8225.

(9) R. J. Hovey, J. J. O'Connell and A. E. Martell, THIS JOURNAL, 81, 3189 (1959).

(10) T. Moeller, ed., "Inorganic Syntheses," Vol. V, McGraw–Hill Book Co., New York, N. Y., 1959, p. 113.

TABLE I

VAPOR PRESSURES OBSERVED FOR THE COMPLEXES $VO(C_5H_7O_2)_2 \cdot B$

B = Ammonia		Methylamine		Ethylamine		Isopropylamine		t-Butylamine	
T (°K.)	P (mm.)	T (°K.)	P (mm.)	T (°K.)	P (mm.)	T (°K.)	P (mm.)	T (°K.)	P (mm.)
305.7	6.6	309.5	2.4	324.3	9.7	305.7	12.5	278.8	2.7
308.9	8.2	313.2	3.0	328.6	31.1	314.0	28.5	280.7	3.6
314.9	13.3	315.2	3.2	329.0	32.7	320.1	46.9	297.2	16.4
321.4	22.0	329.2	10.4	335.5	47.8	324.8	69.3	299.2	20.9
332.1	47.7	332.1	13.9	339.1	56.7	330.1	98.5	302.2	31.8
337.0	65.3	333.9	17.1	344.8	102.1	334.0	126.4	303.2	37.4
340.7	81.2	335.4	18.4	346.4	108.8	340.3	203.9	304.3	38.6
346.5	118.8	340.8	27.6	351.2	137.6				
		344.1	32.8						

inches in length, of potassium or sodium hydroxide) was passed through a sample of the complex, which was loosely packed in a cylindrical tube, until the color had changed completely. The second method, used where the amine existed as a liquid at room temperature, involved merely mixing the liquid amine with a slight stoichiometric excess of the solid complex. In every case there was an easily observable color change from the turquoise of the original complex to the medium to dark green color of the adduct. The combination appeared to occur without any expansion of the solid. These preparations were identical in physical and chemical properties with those reported earlier in the literature.[7,11]
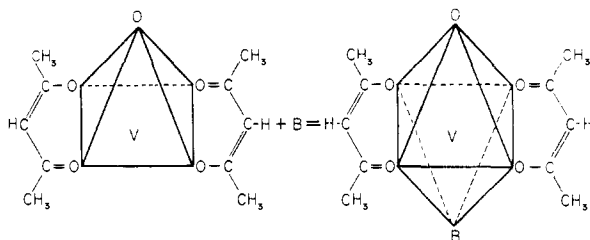

Fig. 1.

Vapor Pressure Measurements.—The vapor pressure measurements were carried out in a simple vacuum system fitted with a mercury manometer. The manometer was read, using a cathetometer, to ± 0.1 mm. The sample was immersed in an oil-bath whose temperature was regulated to ± 0.05° by means of a thermoregulator. For readings below room temperature this same apparatus was used in conjunction with a refrigeration unit. One-half hour was allowed for the establishment of equilibrium after the system had been evacuated. That the dissociation processes were completely reversible was demonstrated by (1) the reproducibility of pressures for a given amine adduct at a given temperature using several different preparations and (2) the identical values of pressure obtained for a given amine adduct at a given temperature when approached from a higher and a lower temperature.

Results and Discussion

The vapor pressure measurements are summarized in Table I. The thermodynamic constants derived from the measurements with reference to the dissociation equations described earlier and the hypothetical one atmosphere reference state are listed in Table II.

In addition, reactions with other amines were examined. Neither triethylamine nor diethylamine gave any evidence of reaction. The apparatus was unsuitable for the study of the adducts with n-propylamine, pyridine, aniline, cyclohexylamine, allylamine and n-butylamine because the amine condensed on those parts of the system which were at room temperature. The adducts with pyrrolidine and pyrrole decomposed on standing. It

(11) A. Rosenheim and Hsing Yu Mong, Z. anorg. Chem., 148, 34 (1925).

TABLE II

THERMODYNAMIC CONSTANTS FOR THE REACTIONS

B = Amine	ΔH^0_{298} (cal./ mole)	ΔF^0_{298} (cal./ mole)	ΔS^0_{298} (cal./ mole/ deg.)	$K_{p,298}$ (mm.)
Ammonia	15,100	3210	40.0	3.40
Methylamine	16,800	4080	42.7	0.779
Ethylamine	16,000	3370	42.4	2.55
Isopropylamine	15,800	2740	43.8	7.48
t-Butylamine	17,500	2120	51.6	21.2

appeared in this latter instance that the vanadium had oxidized the pyrrole. While an adduct with chloroform has been reported,[11] no evidence of reaction was noted on (1) mixing chloroform with the vanadyl chelate or (2) refluxing the vanadyl chelate in an excess of chloroform.

A comparison of these values with those found for the molecular addition compounds involving boron[3] shows a number of interesting similarities. In the first place, the standard enthalpy values are of comparable magnitude, running from 15 up to 17.5 kcal./mole for the vanadium compounds and from 13.75 to 23.48 kcal./mole for the compounds with boron trimethyl. Secondly, the standard entropy effects are found to be of the same order of magnitude, i.e., 40–50 e.u., and, in general, dissociation in the vanadium complexes is attended by very nearly the same entropy change as is found for the corresponding boron trimethyl complexes. The ΔS^0 data show this remarkable similarity

|	Ammonia	Methyl- amine	Ethyl- amine	Iso- propyl- amine	t-Butyl- amine
$VO(C_5H_7O_2)_2 \cdot M$	40.0	42.7	42.4	43.8	51.6
$(CH_3)_3B \cdot M$ (ref. 3)	39.9	40.6	43.0	39.3	44.7

Obviously the differences in the restraints on the amines are not greatly different in the solid vanadium complex or in the gaseous boron complex. This is certainly unexpected and seems to indicate the fundamental similarities to be found when the coördination act of a ligand is studied in isolation from solvation effects. The slight differences noted with the larger ligands probably are due to variations in rotational entropy losses of the ligand when coördination takes place within the crystal lattice.

The correlation of the free energy changes involved with corresponding base strengths of the amines in water suggests itself as a possibility. Here again the similarity of the vanadium and boron adducts is of some interest. In both cases the ammonia complex is more stable than would be

predicted from the behavior of the amines. The agreement in the trends for the compounds once again illustrates the general similarities of the coördination act in both cases.

It is also of considerable interest to compare these enthalpy values with the quantity calculated on the basis of the crystal field theory for the transition from an octahedral to a square pyramidal configuration for a d^1 system.[12] In the first case, a distorted octahedron is predicted, as is certainly true for the complexes of the ion VO^{+2}. The fact that crystal field theory predicts that the transformation from the regular octahedron to the square pyramidal structure is accompanied by an increased stability is not strictly in accord with the data presented here for this particular d^1 system. The approximations involved in the calculation are certainly important in determining this result, especially the assumption of a regular octahedron. The evidence presented here thus provides proof that the variation of the symmetry may lead to a preferred configuration other than one predicted by such calculations. Thus the effect of the approximations involved in the calculations is sufficiently great to demand caution in evaluating the relative stabilities of two possible configurations.

The results obtained here are also different in several important respects from those reported by Knop and Brubaker,[13] who studied the dissociation pressures of a number of amine complexes of Pt(II) of the general form $[Pt(bipyr)(B)_n]^{+2}$ where B represents various dissociable amines such as ammonia, methylamine, ethylenediamine and 1,3-propanediamine. The dissociation process observed by Knop and Brubaker was different in character, however, as it involved a change in the solid state from an ionic to a molecular solid, i.e.

$$[Pt(bipyr)(B)_n]Cl_2(s) \rightleftarrows [Pt(bipyr)Cl_2](s) + nB$$
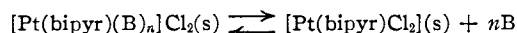
Such a change of necessity must involve a very considerable reorganization in the solid state in addition to changes in the coördination sphere of the platinum. The result of this is that the unambiguous unravelling of the several contributions to the measured over-all thermodynamic changes is quite difficult. The variation in the character of the X-ray powder patterns of the solids, as reported by Knop and Brubaker, is certainly in accord with the possibility of extensive and uncertain structural variations during the reactions studied.

It is also pertinent to consider the entropy changes in more detail and to determine whether a reasonable simple explanation of the very large entropy changes can be obtained. It is imperative to recall that the entropy changes observed for coördination are almost invariably much smaller than those reported either here or in the gas phase work of Brown and his collaborators.[8]

We first note that each reversible reaction being studied here by the vapor pressure method is analogous to a simple phase change in a two-component system whereby the ligand vapor is in

equilibrium with two solid phases. At constant temperature the vapor pressure of the ligand is fixed and ΔF for the equilibrium process is actually zero. This means that for these reactions $\Delta H/T = \Delta S$ at each temperature. Since the plots of $\ln p$ vs. $1/T$ are linear over the temperature ranges studied, ΔH is a constant and the values of ΔS must vary inversely with the temperature. Consequently, all heat absorbed goes into raising the vapor pressure of the ligand. For the ammonia system, over the temperature range 305.7–340.7°K. ΔS changes from 49.5 to 44.4 e.u. thus showing a net change of −5.1 e.u. If we assume ammonia is an ideal gas with a constant C_v value of 6.57 cal./mole deg.,[14] the changes in vapor pressure of the ammonia complex over the same temperature range correspond to a net ΔS change of −4.04 e.u. Therefore about 80% of the decrease in ΔS with temperature for this system can be ascribed to the transfer of ligand from the solid to the gas phase.

That the transfer of a ligand from the solid to the gas phase leads primarily to the release of translational entropy, with some contribution from internal entropy effects as well, is supported by the data presented in Table III. The translational entropies (S^{298}_{trans}) for each vapor were estimated using the Sackur–Tetrode equation and their corresponding absolute entropies (S^0_{298}) were calculated by a standard method.[15]

TABLE III
A COMPARISON OF ENTROPY TERMS

Base	$S^{298}trans$ (e.u.)	S^0_{298} (e.u.)	ΔS^0_{298} (obsd.)(e.u.)
Ammonia	34.6	46.0	40
Methylamine	36.4	57.7	42.7
Ethylamine	37.6	68.1	42.4
Isopropylamine	38.3	71.3	43.8
t-Butylamine	39.0	88.6	51.6

Inasmuch as the rotational entropy makes a major contribution to S^0_{298} with the heavier amines, the ΔS^0_{298} values observed indicate that a considerable amount of this rotational entropy is unaffected by coördination. Such additional possible structural complications as hydrogen bonding seem to be present to only a very slight extent in these compounds.

TABLE IV
THERMODYNAMIC CONSTANTS FOR THE REACTIONS
$$VO(C_5H_7O_2)_2 \cdot B_1 + B_2 \rightleftarrows VO(C_5H_7O_2)_2 + B_2 + B_1$$

B_1	B_2	ΔF^0_{298} (cal./mole)	ΔH^0_{298} (cal./mole)	ΔS^0_{298} (cal./mole/deg.)
Ammonia	Methylamine	− 870	−1700	− 2.7
Ammonia	Ethylamine	− 160	− 900	− 2.4
Ammonia	Isopropylamine	+ 470	− 700	− 3.8
Ammonia	t-Butylamine	+1090	−2400	−11.6
Methylamine	Ethylamine	+ 710	+ 800	+ 0.3
Methylamine	Isopropylamine	+1340	+1000	− 1.1
Methylamine	t-Butylamine	+1960	− 700	− 8.9
Ethylamine	Isopropylamine	+ 630	+ 200	− 1.4
Ethylamine	t-Butylamine	+1250	−1500	− 9.2
Isopropylamine	t-Butylamine	+ 620	−1700	− 7.8

The data obtained by the vapor pressure method also can be used to determine the thermodynamic constants for competitive replacement of one base

(12) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 108–109.

(13) C. P. Knop and C. H. Brubaker, Jr., J. Inorg. Nuclear Chem., 9, 8 (1959).

(14) F. Daniels and R. A. Alberty, "Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 105.

(15) I. M. Klotz, "Chemical Thermodynamics," Prentice–Hall, Inc., New York, N. Y., 1950, pp. 172–177.

by another. These constants are tabulated in Table IV. This table shows the data in a form suitable for the comparison of relative structural effects. The dominating factor seems to be the larger entropy changes as the amines become larger. The free energy changes show the most

regular trends here reflecting the rough ordering according to base strengths mentioned earlier.

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Chelating Tendencies of Some *alpha*-Mercaptoacetamides with Bivalent-Metal Ions

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Acid dissociation constants of several α-mercaptoacetamides and formation constants of some bivalent-metal chelates have been determined. The effects of substitution are discussed.

Introduction

The efficacy of "thionalide,"[1,2] 2-$C_{10}H_7$NHCO-CH_2SH, as an analytical precipitating agent has long been recognized.[3,4] The use of "thionalide" in the volumetric analysis of various metals is discussed by Kolthoff and Belcher.[5]

In view of the usefulness of "thionalide," it would be of interest to study the properties of

pared by the method of Bersin.[7] This consists in the reaction of an equimolar mixture of reactants (amine, NH_4SCN and α-chloroalkanoic acid), hydrolysis of the carbamate thus formed and acidification of the basic solution to obtain the mercaptoacetamide. The preparation of 2-mercapto-N-butyramide (VI) represents a typical preparation except that an α-bromo acid was used as a reactant.

$CH_3CH_2CH(SH)CONHC_6H_5$.—A mixture of aniline (18.6 g., 0.2 mole), α-bromobutyric acid (33.4 g., 0.2 mole) and NH_4SCN (14.2 g., 0.2 mole) in 50 ml. of 95% ethanol was

TABLE I

MERCAPTOACETAMIDES[8] OF THE TYPE ArNHCOCH(SH)R

Compound No.	Ar	R	Yield, %	M.p., °C	Recryst. solvent[a]	Mol. wt. Calcd.	Mol. wt. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
I	C_6H_5	H	..		..	167.23	170[d]	...	...	..	..	..	..
II	4-$CH_3C_6H_4$	H	61	126–128[e]	A	181.26	180	59.63	59.38	6.12	5.83	7.73	7.72
III	2,5-$(CH_3O)_2C_6H_3$	H	52	88–90	A	227.35	227	52.83	52.78	5.76	5.53	6.19	6.33
IV	2,6-$(CH_3)_2C_6H_3$	H	24	129–131[f]	A	195.28	199	61.50	61.85	6.71	6.72	7.18	7.39
V	2,6-$(C_2H_5)_2C_6H_3$	H	8	118–120[g]	B	223.34	225	64.54	64.82	7.67	7.47	6.28	6.38
VI	C_6H_5	C_2H_5	46	95.5–97[g]	B	195.28	194	61.50	61.55	6.71	7.00	7.18	6.90

[a] A, 50–75% ethanol: B, benzene–petroleum ether (b.p. 90–110°). [b] Purchased from Eastman Kodak Company. [c] Reported m.p. 110°, ref. 7. [d] Iodimetric titration, ref. 5. [e] Reported m.p. 126°, ref. 6. [f] Reported m.p. 129°, ref. 6. [g] Reported m.p. 95° [H. Beckurts and G. Frerichs, *J. prakt. Chem.*, [2] 66, 172 (1902)].

other mercaptoacetamides. A number of such compounds and their gold(I) derivatives have been prepared by Weiss,[6] and the preparation of 2-mercaptoacetanilide (I) and its cobalt salts have been reported by Bersin.[7] However, the dissociation constants of mercaptoacetamides and formation constants of the metal derivatives appear never to have been determined. In this communication, such data are reported.

Experimental[8]

Preparation of Mercaptoacetamides. (Table I).—The ligands, white solids, having a characteristic odor, were pre-

(1) 2-Mercapto-N-2-naphthylacetamide.

(2) The names and corresponding numbers of the compounds prepared for this study are: 2-mercapto-N-phenylacetamide, I; 2-mercapto-N-(4-methylphenyl)-acetamide, II; 2-mercapto-N-(2,5-dimethoxyphenyl)-acetamide, III; 2-mercapto-N-(2,6-dimethylphenyl)-acetamide, IV; 2-mercapto-N-(2,6-diethylphenyl)-acetamide, V; 2-mercapto-N-phenylbutyramide, VI.

(3) R. Berg and W. Roebling, *Z. angew. Chem.*, 48, 430 (1935).

(4) For a summary of pertinent references see: J. H. Yoe and L. A. Sarver, "Organic Analytical Reagents," John Wiley and Sons, Inc., New York, N. Y., 1945, pp. 155, 258.

(5) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957, pp. 391–393.

(6) U. Weiss, THIS JOURNAL, 69, 2684 (1947).

warmed. The solution became yellow as a white solid precipitated and vigorous refluxing began. The mixture was quickly poured over ice, and a yellow-white solid crystallized.[9] The carbamate was collected, air-dried (wt., 31 g.), then ground with about 50 ml. of concd. NH_4OH. The filtered hydroxide solution was acidified (1:2 HCl) at 0–10°. The resulting white solid was collected, dried (wt., 18.0 g.) and recrystallized.

Potentiometric Titrations.—Acid dissociation constants in dioxane–water mixtures were determined by the method of Van Uitert,[10] using tetramethylammonium hydroxide. Potentiometric titrations were performed as previously described.[11] Formation constants were calculated using the method of Block and McIntyre.[12]

Discussion

Acid Dissociation Constants.—The pK_D values of the mercaptoacetamides were determined as a function of mole fraction of dioxane (N_2) at 30°. Mathematical expressions for the linear pK_D-N_2

(7) T. Bersin, *Z. anal. Chem.*, 85, 428 (1931).

(8) Microanalyses were performed at the University of Illinois by Mrs. A. Bay, Miss J. Liu and Mr. J. Nemeth.

(9) Usually the carbamate crystallized at once, but the carbamate of V was obtained as an oil.

(10) (a) L. G. Van Uitert, *et al.*, THIS JOURNAL, 75, 455 (1953); (b) *ibid.*, 76, 5887 (1954).

(11) L. G. Van Uitert, *et al.*, *ibid.*, 75, 457 (1953).

(12) B. P. Block and G. H. McIntyre, Jr., *ibid.*, 75, 5667 (1953).