Å.,[38,39] $p = 2/3$, and $\beta = -2.6_6$ e.v. for benzene as mentioned above. The results are shown in the last column of Table III. On the other hand, the observed ratio of the diamagnetic anisotropies of the two compounds is $36/54 = 0.67$. Interpolation by means of Table III gives $d = 1.0_5$, $q_B = 0.24$, $p_{BN} = 0.45$ and $\beta_{BN} = -2.3_1$ e.v. for the molecular parameters of a borazole ring.

The value of d is in excellent agreement with that given by Roothaan and Mulliken,[8] 1.0. The resulting value of $\alpha_N - \alpha_B = -4.7$ e.v. compares favorably with $\alpha_N - \alpha_C = -(1.8\text{–}2.4)$ e.v.[40] The value of β thus obtained gives the ratio, $\beta_{\text{boraz}}/\beta_{\text{benz}} = 2.31/2.66 = 0.87$ in good agreement with the ratio of overlap integrals, $s_{\text{boraz}}/s_{\text{benz}} = 0.219/0.25 = 0.88$. It is known[31] that β (or the resonance integral) of CC bonds varies with the interatomic distance in proportion to the overlap integral s. The present results confirm that the same relation is valid also for bonds involving heteroatoms.[41]

The extent of contribution of the donor–acceptor double bond structure, *i.e.*, the π-electron distribution q_B on boron atoms in a borazole molecule has been a subject of considerable dispute. Although the marked similarity of a borazole ring to a benzene ring suggests a fairly high value of q_B, the present analysis gives 0.24 in agreement with the conclusion derived by Pease[42,43] from observed interatomic distances that q_B is not very great. Rector, *et al.*,[7] have estimated the value of q_B at about 0.15 from the observed BN bond distance. However, since no reliable data are available at present for the single bond distance as well as the double bond distance of BN bonds, the value thus obtained is open to question. On the other hand, Kobayashi[44] has carried out SCF m.o. treatment on borazole and found $q_B = 0.52$.

The evaluation of the dependence of bond lengths upon the bond order of bonds between different atoms presents considerable difficulties owing to the lack of sufficient data.[45,46] The π-electron bond order $p_{BN} = 0.45$ for a BN bond distance $r_{BN} = 1.44$ Å. for borazole is consistent with the curve of CC bond lengths plotted against the bond order and suggests the adequacy of the values for the single bond distance ($r_s = 1.56$ Å.) and the double bond distance ($r_d = 1.35$ Å.) proposed by Coffin and Bauer[5] and those by Cartmell and Fowles[47] ($r_s = 1.54$, $r_d = 1.36$ Å.). On the other hand, the values of BN distances given by Rector, *et al.*,[7] ($r_s = 1.48$, $r_d = 1.30$ Å.) and by Hedberg and Stosick[48] ($r_s = 1.49$ Å.) deviate appreciably from the curve of CC bond lengths mentioned above.

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[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES, PITTSBURGH 35, PENNSYLVANIA]

The Sulfur Hexafluoride Clathrate of Dianin's Compound (4-*p*-Hydroxyphenyl-2,2,4-trimethylchroman): Preparation, Characterization and Thermal Decomposition

BY L. MANDELCORN, N. N. GOLDBERG AND R. E. HOFF

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The sulfur hexafluoride clathrate of Dianin's compound is obtained by recrystallization at a high pressure of sulfur hexafluoride. The amount of sulfur hexafluoride contained in the clathrate so prepared is about 13% by weight, which on the basis of volume of containing solid, is equivalent to a pressure of 25 atmospheres of gas. At temperatures below its melting point, this clathrate decomposes by sublimation of Dianin's compound. The decomposition rate is limited by the ratio of sample volume to exposed area and by the magnitude of external gas pressure. An examination of infrared spectra reveals that chemical interactions between the sulfur hexafluoride and its enclosing cages are very slight. Evidence that the guest-free form of Dianin's compound also possesses the clathrate structure is derived from density measurements.

Introduction

A review of the subject of clathrates[1] mentioned that these substances afford a convenient means for storage and for controlled release of inert gases. Generally, in clathrate systems, gases are retained under ordinary conditions and may be released easily by simple processes such as heating, dissolving or grinding. Sulfur hexafluoride is a gas that has found considerable use in electrical devices. It was felt that its range of practical applicability would be considerably enhanced if it were associated with a solid. A clathrate of sulfur hexafluoride appeared to fulfill this requirement.

Dianin's compound was selected as the host component for a clathrate of sulfur hexafluoride as a result of preliminary reports by Baker and McOmie[2] and by Powell and Wetters[3] on an extensive investigation of the properties of this solid. They showed that three series of clathrates of Dianin's compound are possible; their maximum-composition formulas being $6C_{18}H_{20}O_2 \cdot 3M_1$, $6C_{18}H_{20}O_2 \cdot 2M_2$ and $6C_{18}H_{20}O_2 \cdot M_3$ where M_1, M_2 and M_3 are molecules of the size of methanol, ethanol and hexachloroethane, respectively. Since the size of a sulfur

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(1) L. Mandelcorn, *Chem. Revs.*, **59**, 827 (1959).

(2) W. Baker and J. F. W. McOmie, *Chem. & Ind.* (*London*), 256 (1955).

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TABLE I

SOME PROPERTIES OF DIANIN'S COMPOUND AND TWO OF ITS CLATHRATES

	Dianin's comp.	Ethanol clathrate	Sulfur hexafluoride clathrate
Composition	$C_{18}H_{20}O_2$	$6C_{18}H_{20}O_2\cdot 2C_2H_5OH$	$\sim 6C_{18}H_{20}O_2\cdot 1.7SF_6$
Melting point, °C.	158–159	165–166	163–165
Density, g./cc.	1.15	1.19	1.30 ($6C_{18}H_{20}O_2\cdot 1.79SF_6$)
Infrared spectra	[a]		[a] Similar to $C_{18}H_{20}O_2$ but added absorption band at 938 cm.$^{-1}$
Thermal stability			After 3 yr. <0.5% decomp. at room temp. and atm. pressure

[a] ADI Document No. 6123. The Library of Congress, Photoduplication Service.

hexafluoride molecule is in the range of M_2, it was felt that a clathrate of this gas with a maximum-composition formula $6C_{18}H_{20}O_2\cdot 2SF_6$ is possible. The highest content of sulfur hexafluoride in this clathrate, on a weight percentage basis, is therefore 14.7. According to the procedure presented here, a product was obtained which contained about 13% by weight sulfur hexafluoride.

Experimental

The ethanol clathrate of Dianin's compound was synthesized according to a procedure given by Baker, *et al.*[4]

Guest-free Dianin's Compound.—This modification of Dianin's compound was prepared by vacuum (5 mm.) recrystallization of the ethanol clathrate using decanol or dodecanol as a solvent. A one to one weight ratio of solute to solvent was used and the recrystallization took place in the temperature range of 140° to room temperature. The guest-free crystals were washed with dodecane or heptane and finally dried by suction.

Sulfur Hexafluoride Clathrate of Dianin's Compound.—The ethanol clathrate of Dianin's compound (100 g.) was dissolved at 130–140° in dodecanol or decanol (100 g.) and the solution was evacuated to remove the ethanol. The hot solution was then transferred to an autoclave which was kept at 130–140°. After the autoclave and its contents were flushed with sulfur hexafluoride, the pressure was raised to 300–350 lb. per in.^{2} sulfur hexafluoride (the pressure of liquid sulfur hexafluoride at room temperature). The solution then was cooled to room temperature in 4 to 5 days during which time the solution was constantly subjected to the high pressure and continuously stirred. At the end of the cooling period, a dense slurry of crystallized solid was found in the autoclave. The solid was removed and quickly freed from liquid by suction in a Buchner funnel. A process of one or two washings with a hydrocarbon solvent such as heptane or dodecane (in which Dianin's compound is slightly soluble) and suction drying removed most of the remaining solvent from the solid. This solid (about 90 g.), the clathrate, was found to consist of about 13% by weight of sulfur hexafluoride. Analyses were made by melting the clathrate and determining the amount of gas released by means of either a mass spectrometer or a conventional gas-measuring apparatus.

When the sulfur hexafluoride pressure was about one atmosphere during recrystallization, products were obtained which were found to consist of about 6% by weight sulfur hexafluoride and, in one instance, 9%.

Infrared Spectra.—The KBr pellet technique was used to obtain the spectra of the guest-free modification and the sulfur hexafluoride clathrate of Dianin's compound. A Perkin-Elmer Model 21 Infrared Spectrophotometer was used and the samples were scanned over the range of 650 to 4000 cm.$^{-1}$

Thermal Decomposition at 0.1 to 30 mm. Pressure.—The apparatus used for the study of the thermal decomposition of the sulfur hexafluoride clathrate of Dianin's compound was a vacuum system, consisting of a two-stage Welch pump, a cold trap, a mercury manometer and a vertical hot finger which was immersed in a temperature-controlled oil-bath. The manometer, together with the cold trap, could be isolated by means of two stopcocks for the determination of sulfur hexafluoride evolved during decomposition. The clathrate was ground into a fine powder in a mortar or in a ball mill. About 300 to 500 mg. of this powder was weighed into a glass vial (0.4 cm. i.d.) into which some bits of iron wire and a glass wool plug were then placed. While the system was being evacuated and the hot finger heated, the sample was located in a horizontal portion of the tubing adjacent to the hot finger. The sample was dropped into the vertical hot finger by moving it with a magnet which attracted the iron wire.

In one series of experiments, the pressure of evolved sulfur hexafluoride was allowed to build up over the decomposing sample. The decomposition was followed for a period of 2 hr. at the end of which the pressure was about 10 mm. at the lowest temperature studied (99°) and 30 mm. at the highest temperature (155°). Other experiments were made with the pressure kept, during decomposition, at about 0.1 mm. (the limit of the Welch pump). Here, evolved sulfur hexafluoride was condensed in the trap cooled with liquid nitrogen and periodically determined manometrically. Weight loss data (for the purpose of determining the amount of Dianin's compound sublimed) were obtained for a series of different samples decomposed for varying periods of time at 160°.

Thermal Decomposition at 10^{-5} mm.—The evacuated portion of the apparatus used in these experiments was free of mercury and of grease. The apparatus consisted of a two-stage mercury diffusion pump and an ionization gauge (to measure pressure) as well as a large cold trap, which was located between the diffusion pump and the hot finger and which was cooled with liquid nitrogen. Small samples of clathrate (10 to 70 mg.) were weighed into a platinum boat and larger ones into a glass cylinder. Both sample holders were 1 cm. in diameter. For a decomposition experiment, the sample was lowered into the hot finger through an opening in the glass tubing. The opening was sealed by fusing the glass, and the system was evacuated and degassed for more than 12 hr. Heat for degassing was supplied by heating tape which was wrapped around all the exposed glass tubing except that portion where the sample was located. On removal of the tape, the pressure was less than 10^{-6} mm. The controlled bath then was moved into position to heat the sample. The pumps operated throughout the entire period of the decomposition and the pressure never rose above 10^{-4} mm. After the decomposition, the sample was weighed and analyzed mass-spectrometrically for sulfur hexafluoride. From the weight loss and analytical data, the amounts of sulfur hexafluoride and of Dianin's compound evolved were determined.

Results and Discussion

Some of the properties of Dianin's compound and of the ethanol and sulfur hexafluoride clathrates are summarized in Table I. According to the density figures, the mass of Dianin's compound per unit volume is the same in both clathrate and non-clathrate forms. The composition of the sulfur hexafluoride clathrate falls short of two molecules of sulfur hexafluoride per unit cage cell, probably because of the limited solubility of sulfur hexafluoride in the crystallizing solutions. These two properties are consistent with the ideas that guest-free Dianin's compound is similar structurally to the clathrate form[3] and that a single cage cell of six molecules of Dianin's compound can retain two of sulfur hexafluoride.

The added infrared absorption maximum for the sulfur hexafluoride clathrate at 938 cm.$^{-1}$ is of interest since it corresponds to one of the fundamental vibration frequencies of sulfur hexafluoride gas, reported as 940[5] and 932 cm.$^{-1}$.[6] Apparently,

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(4) W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving and J. H. Wild, *J. Chem. Soc.*, 2010 (1956).

the interaction between the sulfur hexafluoride and its enclosing cages is so weak that the vibrational energy of this clathrated sulfur hexafluoride is the same as that of the free gas.

It was always observed, during the various decompositions of the sulfur hexafluoride clathrate of Dianin's compound, that some of the solid, Dianin's compound, sublimed into the cold portions of the apparatus. The purpose of the experiments at 10^{-5} mm. was to allow the sublimation to proceed without hindrance of external gas. Such hindrance can be significant at pressures greater than 10^{-3} mm. where the mean free path of gas molecules is small.

Table II summarizes some of the results obtained at various pressures and temperatures for decomposition periods of two hours. In Tables III and IV the amounts of sulfur hexafluoride evolved and of Dianin's compound sublimed are given for decompositions at 10^{-1} and 10^{-5} mm. for 160 and 100°, respectively. At the lowest pressure, the rates of decomposition at 130 and 140° of 10 mg. samples were about six-fold that at 100°.

TABLE II

THERMAL DECOMPOSITION OF THE SF_6 CLATHRATE OF DIANIN'S COMPOUND

Original Sample Weight = 300–500 mg.
Decomposition Time = 2 hours

	Temp., °C.	Clathrated SF_6 evolved, %
(a) External press. >1 mm.	99	4
	128	11
	155	16
(b) External press. ~0.1 mm.	125	12
	150	20
	160	41
(c) External press. $\sim 10^{-5}$ mm.	100	9

TABLE III

THERMAL DECOMPOSITION OF THE SF_6 CLATHRATE OF DIANIN'S COMPOUND AT 160° AND 0.1 MM.

Initial sample, mg.	Time, hr.	—Weight loss, mg.— $C_{18}H_{20}O_2$	SF_6	$\frac{\text{Wt. loss } SF_6}{\text{Wt. loss } C_{18}H_{20}O_2}$
480.0	1	49.9	14.06	0.28
463.1	2	89.2	23.95	.27
479.7	2.5	162.0	32.57	.20
523.4	3.5	248.6	40.60	.164
447.7	4	248.1	40.02	.162
470.4	12	411.0	59.45	.144

TABLE IV

THERMAL DECOMPOSITION OF THE SF_6 CLATHRATE OF DIANIN'S COMPOUND AT 100° AND 10^{-5} MM.

Initial Sample, $\frac{\text{Wt. } SF_6}{\text{Wt. } C_{18}H_{20}O_2} = 0.13$

Initial sample, mg.	Time, hr.	—Weight loss, mg.— $C_{18}H_{20}O_2$	SF_6	$\frac{\text{Wt. loss } SF_6}{\text{Wt. loss } C_{18}H_{20}O_2}$
9.992	1	1.24	0.35	0.28
33.8	1	1.0	.17	.17
9.980	1.5	4.032	.59	.5
35.3	1.5	4.3	2.14	.5
9.891	2	5.72	0.81	.14
35.0	2	4.5	1.13	.25
75.0	2	7.6	1.10	.15
297.1	2	10.5	4.0	.38
405.7	2	5.8	4.9	.85

The decomposition of the clathrate was found to be affected by the physical characteristics of the samples, such as particle size and packing of the powder. Samples consisting of large particles or densely packed powders decomposed more slowly than did those which were finely ground or loosely packed. Those factors could not always be controlled or specified precisely. The data given here serve to illustrate in a qualitative manner the effects of temperature, pressure and sample size on the rate of decomposition of the clathrate.

The significant experimental results can be summarized as:

(1) A decrease in the external pressure causes an increase in the rate of evolution of sulfur hexafluoride.

(2) The rates of evolution of sulfur hexafluoride and Dianin's compound, per unit weight of initial sample, decrease with increasing sample size.

(3) The weight ratio of evolved sulfur hexafluoride to sublimed Dianin's compound is greater than the ratio of these components in the original sample.

(4) This ratio increases with increasing sample size.

(5) Generally, this ratio decreases with increasing decomposition time.

Four different processes are possible in the thermal decomposition of a clathrate[1]: sublimation of the host, diffusion of the guest component through the clathrate structure, rearrangement of the crystalline structure and desorption of the guest component from the surface. Sublimation is obviously a major process occurring in the thermal decomposition of the sulfur hexafluoride clathrate of Dianin's compound. Concerning the other three processes, all of them should not be affected by sample size. Furthermore, even by increasing the external pressure from 10^{-5} to 50 mm., the concentration differential (between the solid and gas phases) of sulfur hexafluoride is not sufficiently changed to affect a diffusion controlled process.

If the sublimation of Dianin's compound is unhindered (*i.e.*, if every molecule leaving the surface of a particle escapes from the sample) and if it is the only process in the decomposition of the clathrate, then sulfur hexafluoride and Dianin's compound would evolve in the same ratio as that of the solid sample. The rate at which molecules leave the surface of a particle depends only on temperature. However, recondensation of evolved solid molecules on the sample itself can occur when the mean free path of a molecule is small (at pressures greater than 10^{-3} mm.) and when upper layers of sample particles are in the path of evolved molecules. Essentially, the sample is a self-adsorption barrier to free passage of molecular Dianin's compound. Readsorbed Dianin's compound will assume the form of a protective coating on the particles and will hinder the evolution of sulfur hexafluoride by sublimation of clathrate crystals. On the other hand, sulfur hexafluoride molecules, once liberated by sublimation of the encaging host,

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(5) R. T. Lagemann and E. A. Jones, *J. Chem. Phys.*, **19**, 534 (1951).

(6) J. Gaunt, *Trans. Far. Soc.*, **49**, 1122 (1953).

will escape entirely. This last point was proved in an experiment where guest-free Dianin's compound, after being exposed at 100° for five days to one atmosphere of sulfur hexafluoride, took up only a trace of the gas.

The enumerated experimental observations are adequately explained in accordance with the assumption that the thermal decomposition of the sulfur hexafluoride clathrate proceeds only by sublimation of the host component. Since in all the experiments of this investigation there was hindrance to the escape of Dianin's compound (at least because of the bulk of the sample), the evolution of sulfur hexafluoride also was suppressed as a result, these effects increasing with increasing sample size and pressure. However, the suppression of sulfur hexafluoride evolution occurs to a lesser extent than that of Dianin's compound because the formation of an effective protective coating occurs only as a result of the decomposition of clathrate. Therefore, the total weight ratio of evolved sulfur hexafluoride to evolved Dianin's compound is always greater than the ratio of these components and increases with increasing external pressure or increasing sample size, since the major effect of these two factors is to suppress the escape of Dianin's compound. However, this ratio should decrease with increasing decomposition time as was generally, but not always, observed. A decomposing sample decreases in size (thereby facilitating the evolution of Dianin's compound) and acquires a more effective protective coating, which in turn suppresses the evolution of sulfur hexafluoride. Reduction of the ratio of sulfur hexafluoride to Dianin's compound in a decomposing sample is not a factor because this ratio was always close to the original ratio, the greatest decrease observed being 12%.

The complicating features that surround the proposed sublimation mechanism tie in with the powdered nature of the samples. However, since information was not obtained on the geometry of the particles composing the powders, a strict kinetic analysis of the analytical data could not be made.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WEST VIRGINIA UNIVERSITY, MORGANTOWN, WEST VIRGINIA]

Metal Ion Complexes of N,N'-Bis-(2-hydroxyethyl)-ethylenediamine. Reaction of the Copper(II) Complexes with Sodium Hydroxide[1]

BY JAMES L. HALL AND WARREN E. DEAN

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In solution N,N'-bis-(2-hydroxyethyl)-ethylenediamine, $HO(CH_2)_2NH(CH_2)_2NH(CH_2)_2OH$,[2] forms complexes with copper(II) ion in the ratio Cu(II):hen$(OH)_2$ of 1:1 and 1:2. The reaction of these complexes with more amine and with sodium hydroxide in solution has been studied by spectrophotometric and conductometric methods. The 1:1 complex, $Cu[hen(OH)_2]^{+2}$, reacts with an equivalent amount of sodium hydroxide to form $Cu[hen(OH)(O^-)]^{+1}$ and with two equivalents of sodium hydroxide to form $Cu[hen(O^-)_2]^0$. These latter two complexes may be formed partially by action of an excess of the amine. By comparison with the copper(II) complexes of ethylenediamine, a monoalkanol-substituted ethylenediamine and a tetraalkanol-substituted ethylenediamine, it is shown that the range of *p*H over which the 1:2 complexes are stable decreases with the degree of alkanol substitution. The 1:1 complexes are more stable as the degree of substitution is increased, but this evidently is due to the increased opportunity for formation of chelate rings involving the hydroxyl oxygen atoms.

Introduction

Previous reports from this Laboratory have described the copper(II) complexes of a monoalkanol-substituted ethylenediamine,[3] 2-(2-aminoethylamino)-ethanol (hydroxyethylethylenediamine) and of a tetralkanol-substituted ethylenediamine,[4] N,N,N',N' - tetrakis - (2 - hydroxypropyl) - ethylenediamine. The present study of the copper(II) complexes of N,N'-dihydroxyethylethylenediamine was undertaken with the expectation that a comparison of the three systems would lead to some generalizations relating the degree of alkanol substitution of the ethylenediamine molecule to the type of complexes formed under various degrees of alkalinity.

No previous detailed studies of the metal-ion complexes of hen$(OH)_2$ have been reported. Martell, Chaberek, Courtney, Westerback and Hyytiainen[5] have reported the results of titration with strong base of 1:1 mixtures of copper(II) nitrate and this amine, giving the formation constant of the 1:1 complex and the equilibrium constant for the reaction of the 1:1 complex with strong base. More recently, in a report made after completion of the present work, Courtney, Gustafson, Chaberek and Martell[6] have shown that 1:1

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(1) Sponsored by the Office of Ordnance Reseaıch, U. S. Army. From a portion of the Ph.D. Dissertation of W. E. Dean, West Virginia University, 1959.

(2) To be abbreviated hen$(OH)_2$. Ethylenediamine will be abbreviated en and hydroxyethylethylenediamine will be abbreviated hen(OH).

(3) J. L. Hall and W. E. Dean, THIS JOURNAL, **80**, 4183 (1958).

(4) J. L. Hall, F. R. Jones, C. E. Delchamps and C. W. McWilliams, *ibid.*, **79**, 3361 (1957).

(5) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiainen, *ibid.*, **79**, 3036 (1957).

(6) R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr., and A. E. Martell, *ibid.*, **81**, 519 (1959).