

scribe their sample as a mixture of  $\text{LuB}_4$  and  $\text{LuB}_6$ . Of the 15 lines of their powder pattern attributed to  $\text{LuB}_6$  only two do not coincide with their  $\text{LuB}_4$  lines. Comparison of their powder pattern with that of a pure sample of  $\text{LuB}_4$  prepared here and with the lattice constants of  $\text{LuB}_4$  given by Stepanova and Zhuravlev<sup>34</sup> indicates that all their lines came from the tetraboride.

Samsonov has reported the preparation of  $\text{ScB}_6$  with the  $\text{CaB}_6$  structure. Of the two different lattice constants for  $\text{ScB}_6$  found in his papers,<sup>3,4</sup> 4.355 kX. and 4.435 Å., the latter appears to be a misprint because in the paper in which it occurs the metal-metal distance is given as 4.35 Å.

In nine scandium boride samples prepared in the present work no  $\text{ScB}_6$  was observed, the products consisting of  $\text{ScB}_2$  and  $\text{ScB}_{12}$ . The samples were prepared from mixtures of oxide and boron designed to yield products ranging from B/Sc = 6 to B/Sc = 20. They were heated from half an hour to two hours at various temperatures from 1350 to 1550°. Samsonov<sup>3</sup> stated that the  $\text{ScB}_6$  appeared in a  $\text{ScB}_2$  sample which had been heated for 9 to 10 hours as a cathode for thermionic emission studies. In the present work a  $\text{ScB}_2$  sample

(34) A. A. Stepanova and N. N. Zhuravlev, *Kristallografiya*, **3**, 94 (1958).

containing some  $\text{Sc}_2\text{O}_3$  was heated for 8 hr. *in vacuo*. The new lines which appeared in the X-ray powder pattern were those of  $\text{ScB}_{12}$ . An additional 8-hr. heating produced no significant change.

In Fig. 3 the lattice constants of the hexaborides derived from the more precise values in the literature<sup>14,21</sup> are plotted against the metallic radii. (The data for Ca and La are those of Johnson and Daane.<sup>29</sup>) Samsonov's<sup>3</sup> value of 4.364 Å. (= 4.355 kX.) for  $\text{ScB}_6$  appears to be remarkably large for such a small atom.

It seems that  $\text{LuB}_6$  and  $\text{ScB}_6$  are unstable and may not exist, thus marking the end of the range of stable hexaborides. In this connection, it is of interest that no metals with smaller radii or larger first and second ionization potentials than Sc and Lu are reported to form hexaborides. In addition, while the larger lanthanides such as La, Pr, Sm, Eu and Yb yield pure hexaborides, the smaller ones usually produce mixtures with tetraborides.

**Acknowledgment.**—We are indebted to Mrs. C. Mackey for her assistance with many X-ray determinations. Thanks are due to D. S. Russell, P. Tymchuck and A. Mykytiuk of the Analytical Chemistry Section for making the spectrographic analyses.

[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA, UNIVERSITA DI FIRENZE, FIRENZE, ITALY]

## The Existence of Tetrahedral $\alpha$ -Branched Bis-(R-N-salicylaldimino)-nickel(II) Chelates

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X-Ray analysis and reflectance spectra data of some solid  $\alpha$ -branched bis-(R-N-salicylaldimino)-nickel(II) complexes indicate that the open chain paramagnetic complexes (R = *i*-propyl, *s*-butyl and *t*-butyl) have an essentially tetrahedral structure, whereas the closed chain diamagnetic complexes (R = cyclopentyl, cyclohexyl and cyclooctyl) have a planar structure. Cryoscopic measurements on these compounds show that solute association is responsible for only a part of the paramagnetism exhibited by all of these complexes when dissolved in inert solvents. Furthermore, while the association becomes almost zero in boiling benzene, the percentage of paramagnetic forms in benzene, *m*-xylene and bibenzyl, as calculated by magnetic measurements, increases steadily with an increase in temperature from 20 to 180°. Spectrophotometric and dielectric polarization data of solutions of these complexes in inert solvents show that a high percentage of the observed paramagnetism results from tetrahedral species in equilibrium with the associated and the planar species. In this conformational equilibrium, the percentage of tetrahedral forms increases with increasing temperature.

### Introduction

The existence of tetrahedral species in solutions of bis-(N-methylsalicylaldimino)-nickel(II) put forward<sup>1</sup> to account for the partial solution paramagnetism in inert solvents of this chelate was rejected on the basis of dipole moment measurements.<sup>2</sup> Later this compound was found to form a buff colored insoluble isomer.<sup>3</sup> This isomer was the first example of a paramagnetic solid compound of the type bis-(salicylaldimino)-nickel(II). Its paramagnetism was attributed to an octahedral structure achieved by intermolecular association in the solid.<sup>3</sup>

This hypothesis was used by Holm to explain both the solution paramagnetism of the diamagnetic N-methyl complex and the paramagnetism of some  $\alpha$ -branched complexes both in solutions of inert solvents and in the solid state.<sup>4</sup>

An X-ray analysis of the *i*-propyl and *s*-butyl-N-salicylaldimino-nickel(II) chelates showed them not to

be polymeric in the solid state but to have instead a tetrahedral structure.<sup>5</sup> Cryoscopic and ebullioscopic measurements on solutions of these and other  $\alpha$ -branched complexes can account for only a part of the solution paramagnetism instead of all of it as was originally suggested.<sup>4</sup>

These findings make it clear that further study on these systems is necessary. This paper reports the investigations of some  $\alpha$ -branched nickel(II) complexes by means of magnetic, spectrophotometric, molecular weight and dipole moment measurements with the aim of elucidating the stereochemistry of these compounds in solutions of non-coordinating solvents.

### Experimental

**Preparation of Compounds.** Nickel(II).—The bis-N-cyclopentyl, bis-N-cyclohexyl-, and bis-(N-cyclooctylsalicylaldimino)-nickel(II) complexes were prepared by refluxing 0.01 mole of bis-salicylaldehydonickel(II) dihydrate with a solution of 0.022 mole of the appropriate amine in 50 ml. of ethanol until the precipitate appeared homogeneous under a microscope. After cooling, the solid was collected on a filter and recrystallized from hot xylene. Green needles resulted which are slightly soluble in chloroform and benzene, and insoluble in petroleum ether.

**Bis-(N-cyclopentylsalicylaldimino)-nickel(II).**—m.p. 162–163°. *Anal.* Calcd. for  $\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_2\text{Ni}$ : N, 6.44; Ni, 13.49. Found: N, 6.51; Ni, 13.37.

**Bis-(N-cyclohexylsalicylaldimino)-nickel(II).**—m.p. 213–215°. *Anal.* Calcd. for  $\text{C}_{26}\text{H}_{30}\text{O}_2\text{N}_2\text{Ni}$ : N, 6.05; Ni, 12.67. Found: N, 6.15; Ni, 12.60.

(5) L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962).

(1) J. B. Willis and D. P. Mellor, *J. Am. Chem. Soc.*, **69**, 1237 (1947); H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955) and 520 (1956).

(2) L. Sacconi, P. Paoletti and G. Del Re, *J. Am. Chem. Soc.*, **79**, 4062 (1957).

(3) L. Sacconi, P. Paoletti and R. Cini, Fourth International Conference on Coordination Chemistry, Rome, September, 1957, *J. Inorg. Nucl. Chem.*, **8**, 492 (1958); *J. Am. Chem. Soc.*, **80**, 3583 (1958).

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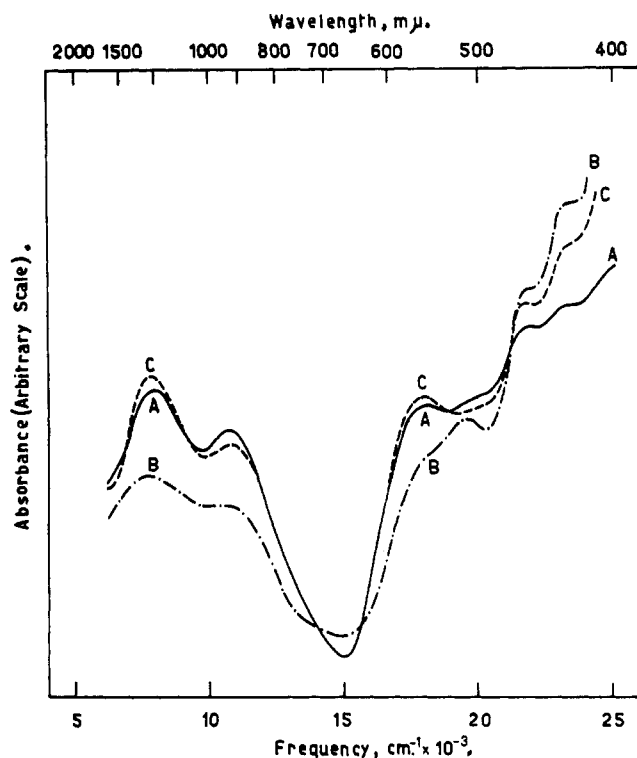


Fig. 1.—Reflectance spectra of bis-(*N*-*i*-propylsalicylaldimino)-cobalt(II) (A), bis-(*N*-*n*-butylsalicylaldimino)-cobalt(II) (B) and bis-(*N*-*s*-butylsalicylaldimino)-cobalt(II) (C).

**Bis-(*N*-cyclooctylsalicylaldimino)-nickel(II).**—m.p. 184–185°. *Anal.* Calcd. for  $C_{36}H_{40}O_2N_2Ni$ : N, 5.39; Ni, 11.30. Found: N, 5.61; Ni, 11.15.

The bis-*N*-*i*-propyl- and bis-(*N*-*s*-butylsalicylaldimino)-nickel(II) complexes were obtained by refluxing 0.010 mole of bis-salicylaldehydonickel(II) dihydrate with a solution of 0.022 mole of the amine in 25 ml. of methanol until solution was complete. The solvent was then evaporated under reduced pressure and the solid recrystallized from cyclohexane. Dark brown plates were formed which are very soluble in chloroform, benzene, ethanol and methanol, and fairly soluble in cyclohexane and petroleum ether.

**Bis-(*N*-*i*-propylsalicylaldimino)-nickel(II).**—m.p. 205–207°. *Anal.* Calcd. for  $C_{20}H_{24}O_2N_2Ni$ : N, 7.32; Ni, 15.33. Found: N, 7.53; Ni, 15.58.

**Bis-(*N*-*s*-butylsalicylaldimino)-nickel(II).**—m.p. 143–145°. *Anal.* Calcd. for  $C_{22}H_{26}O_2N_2Ni$ : N, 6.82; Ni, 14.27. Found: N, 6.98; Ni, 14.17.

The bis-(*N*-*t*-butylsalicylaldimino)-nickel(II) complex was prepared by stirring vigorously a paste of bis-salicylaldehydonickel(II) dihydrate and an excess of *t*-butylamine at room temperature until a dark brown color resulted. This mixture was extracted with warm cyclohexane and the deep brown filtrate was evaporated to incipient crystallization under reduced pressure. On addition of petroleum ether a heterogeneous solid separated which was purified by sublimation (180°,  $2 \times 10^{-5}$  mm.). The dark brown needles were extremely soluble in chloroform, benzene, cyclohexane, dioxane and ethanol, and fairly soluble in petroleum ether. Traces of moisture in the solvents cause separation of a light green nitrogen-free solid.

**Bis-(*N*-*t*-butylsalicylaldimino)-nickel(II).**—m.p. 202–203°. *Anal.* Calcd. for  $C_{22}H_{26}O_2N_2Ni$ : N, 6.82; Ni, 14.27. Found: N, 6.80; Ni, 14.12.

**Cobalt(II).**—The cobalt chelates were prepared according to the procedure already described for other members of this series.<sup>6</sup> They are red crystalline solids fairly soluble in chloroform, benzene, dioxane, slightly soluble in ethanol, cyclohexane and almost insoluble in petroleum ether. They are not oxidized, even in solution, by atmospheric oxygen nor by hydrogen peroxide. The *i*-propyl (m.p. 234–226°) and *s*-butyl (m.p. 163–164°) compounds were reported earlier.<sup>7</sup>

**Bis-(*N*-*t*-butylsalicylaldimino)-cobalt(II).**—m.p. 210–213°. *Anal.* Calcd. for  $C_{22}H_{26}O_2N_2Co$ : N, 6.81; Co, 14.33. Found: N, 6.82; Co, 14.51.

(6) L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavaiano, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

(7) H. Diehl and T. S. Chao, *Iowa State Coll. J. Sci.*, **22**, 126 (1947); H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962).

**Zinc(II).**—A solution of 0.010 mole of zinc acetate tetrahydrate, 0.020 mole of salicylaldehyde and 0.022 mole of the appropriate amine in 25 ml. of ethanol was refluxed over a period of half an hour. On cooling, yellow crystals separated which were recrystallized from anhydrous benzene. The complexes are fairly soluble in chloroform, benzene and pyridine, slightly soluble in cyclohexane, and almost insoluble in petroleum ether. Moisture in the solvents causes hydrolysis.

**Bis-(*N*-*i*-propylsalicylaldimino)-zinc(II).**—m.p. 230–232°. *Anal.* Calcd. for  $C_{20}H_{24}O_2N_2Zn$ : N, 7.19; Zn, 16.77. Found: N, 6.99; Zn, 16.62.

**Bis-(*N*-*s*-butylsalicylaldimino)-zinc(II).** m.p. 171–172°. *Anal.* Calcd. for  $C_{22}H_{26}O_2N_2Zn$ : N, 6.70; Zn, 15.65. Found: N, 6.63; Zn, 15.73.

**Spectrophotometric Measurements.**—The absorption spectra were recorded with a Beckman DK 2 spectrophotometer equipped with a thermostated cell housing of local design. Temperatures from 60 to 180° were obtained by circulating paraffin oil from a thermostat regulating to  $\pm 0.5^\circ$ . In calculating extinction coefficients, allowance was made for the variation of the density of the solution with the temperature. Benzene and xylene were purified by the standard procedures used for spectrophotometric measurements. Bibenzyl was purified by repeated crystallization from light petroleum. The reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference.

**Magnetic Measurements.**—The apparatus used for magnetic measurements and the experimental technique were described in a previous paper.<sup>8</sup> The Gouy tube was calibrated using freshly boiled distilled water, the specific susceptibility of which was assumed to be  $-0.720 \times 10^{-6}$  at 20°. The measured specific susceptibilities of the solvents were: benzene,  $-0.705 \times 10^{-6}$ ; *m*-xylene,  $-0.725 \times 10^{-6}$ ; bibenzyl,  $-0.696 \times 10^{-6}$  (lit.<sup>9</sup>  $-0.702 \times 10^{-6}$ ,  $-0.721 \times 10^{-6}$ , and  $-0.699 \times 10^{-6}$ , respectively). The diamagnetic corrections, calculated from Pascal's constant,<sup>10</sup> are: *i*-Pr,  $-210 \times 10^{-6}$ ; *s*-Bu and *t*-Bu,  $-234 \times 10^{-6}$ .

**Dielectric Polarization Measurements.**—Measurements of dielectric constants and densities were performed with the apparatus and by the procedure described previously.<sup>11</sup> Solutions of the oxidizable *n*-butyl cobalt(II) complex were made up by weight in a closed  $O_2$ -free system and transferred to the cell and the pycnometer under nitrogen pressure so as to avoid contact with atmospheric oxygen. The specific polarization of the solute at infinite dilution,  $P_{2\infty}$ , was determined by the method of Le Fèvre and Vine.<sup>12</sup> Plots of the density vs. weight fraction were found to be straight lines over the concentration range used, whereas in several instances the corresponding plots of the dielectric constants resembled parabolas more closely.<sup>13</sup>

For complexes of cobalt(II) and zinc(II), values of the molar refractions for the sodium line,  $R_D$ , were determined experimentally by measuring the refractive indices of the solutions with a Pulfrich refractometer. The molar refractions for the  $\alpha$ -branched nickel(II) chelates were assumed to be equal to those of the *n*-alkyl analogs.

Values of the orientation polarization,  $P_0$ , were calculated by assuming a value of 20%  $R_D$  for the atom polarization. Such a figure, in the case of the *n*-alkyl nickel(II) chelates, allows for the entire difference  $P_{2\infty} - R_D$ .

**Cryoscopic and Ebullioscopic Measurements.**—Cryoscopic measurements were carried out by the conventional method in benzene. Ebullioscopic measurements in benzene were performed with a Sargent apparatus of Cottrell type. Temperatures were read with a 0.01° Beckman thermometer.

## Results and Discussion

**$\alpha$ -Branched Complexes Paramagnetic in the Solid State.**—Powder diagrams and two-dimensional Patterson synthesis have shown that the *i*-propyl and *s*-butyl nickel(II) complexes are isostructural and practically isometric with the cobalt(II) and zinc(II) analogs.<sup>5</sup> The reflectance spectra of the *i*-propyl and *s*-butyl cobalt(II) complexes are identical with that of the *n*-butyl cobalt(II) complex (Fig. 1) which was found to

(8) L. Sacconi, R. Cini, M. Ciampolini and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(9) G. Foex, "Constantes Sélectionnées diamagnetisme et paramagnetisme," Masson and Cie, Paris, 1957.

(10) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956; B. N. Figgis, J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 403.

(11) L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavaiano, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961).

(12) R. J. W. Le Fèvre and H. Vine, *J. Chem. Soc.*, 1805 (1937).

(13) J. W. Smith, "Electric Dipole Moments," Butterworths Publishers Ltd., London, 1955, p. 59.

TABLE I  
MAGNETIC SUSCEPTIBILITY DATA FOR BIS-(R-N-SALICYLAL-  
DIMINO)-NICKEL(II) COMPLEXES IN SOLUTION

R	Solvent	Temp., °C.	Concn., g., %	$\chi_A$ ( $\times 10^3$ )	$\mu_{\text{eff}}$ (B.M.)	% <sup>a</sup> para- mag.
<i>i</i> -Pr		21		4547	3.31	
	Benzene	21	4.264	1997	2.14	42
	Xylene	20	1.242	1673	1.98	36
			1.892	1653	1.98	36
		40	1.242	1520	1.97	35
			1.892	1473	1.93	34
		60	1.892	1379	1.92	34
		80	1.892	1402	2.00	37
	Bibenzyl		2.178	1559	2.04	38
	Xylene	100	1.892	1606	2.20	44
	Bibenzyl		2.178	1626	2.21	45
		120	2.178	1735	2.34	50
		140	2.178	1905	2.52	58
		160	2.178	1902	2.58	61
		180	2.178	1995	2.70	67
<i>s</i> -Bu		24			3.36 <sup>b</sup>	
	Xylene	24	2.837	1642	1.98	36
		80	2.837	1454	2.03	38
	Bibenzyl	120	3.382	1508	2.19	44
<i>t</i> -Bu		182	3.382	1715	2.51	57
		23		4708	3.35	
	Benzene	23	4.541	4351	3.22	95
Cyclopentyl		23		Diamagnetic		
	Xylene	27	0.605	2295	2.36	51
		80	0.605	2238	2.53	59
	Bibenzyl	120	1.538	2108	2.59	62
Cyclohexyl	Bibenzyl	180	1.538	2159	2.81	73
		21		Diamagnetic		
	Xylene	80	0.860	1154	1.81	30
Cyclooctyl	Bibenzyl	120	1.468	1444	2.14	42
		180	1.468	1551	2.38	52
		28		Diamagnetic		

<sup>a</sup> The percentages were calculated by assuming a  $\mu_{\text{eff}}$  value equal to 3.3 B.M. for both the tetrahedral and associated species. <sup>b</sup> Cf. ref. 4.

be tetrahedral.<sup>6,14</sup> Therefore a tetrahedral, even if somewhat distorted structure must be assigned to the solid *i*-propyl and *s*-butyl nickel(II) chelates. This is the first example of a tetrahedral nickel(II) chelate. Actually the sole examples so far known of tetrahedrally coordinated nickel(II) complexes, both as solids and in solution, are those in which this metal is bound to four unidentate ligands.<sup>15</sup>

The reflectance spectra of the  $\alpha$ -branched paramagnetic compounds bis-*N*-*i*-propyl, bis-*N*-*s*-butyl and bis-(*N*-*t*-butylsalicylaldimino)-nickel(II) ( $\mu_{\text{eff}} \approx 3.3$  B.M., Table I) are quite different from those of the diamagnetic *n*-alkyl derivatives. Some of these spectra are reported in Fig. 2. The *i*-propyl complex, as well as the *s*-butyl (not shown in figure), shows crystal field bands with maxima at 6,700, 10,900, 14,100, 16,900 and 19,600  $\text{cm}^{-1}$  and a shoulder near 9,500  $\text{cm}^{-1}$ . The spectrum of the *t*-butyl compound exhibits in addition some small red shifts and some shoulders in the band under 10,000  $\text{cm}^{-1}$ . On the contrary, spectra of the corresponding planar *n*-alkyl complexes show no absorption in the 5,000–12,000  $\text{cm}^{-1}$  region (Fig. 2).

(14) E. Frasson and C. Panattoni, *Z. Krist.*, **116**, 154 (1961).

(15) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958); N. S. Gill and R. S. Nyholm, *ibid.*, 3997 (1959); D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959); F. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960); D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5771, 5774 (1960); F. A. Cotton and D. M. L. Goodgame, *ibid.*, **82**, 2967 (1960); F. A. Cotton O. D. Faut and D. M. L. Goodgame, *ibid.*, **83**, 344 (1961); C. R. C. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton and L. M. Venanzi *J. Chem. Soc.*, 2705 (1961); R. G. Hayter and F. S. Humiec, *J. Am. Chem. Soc.*, **84**, 2004 (1962).

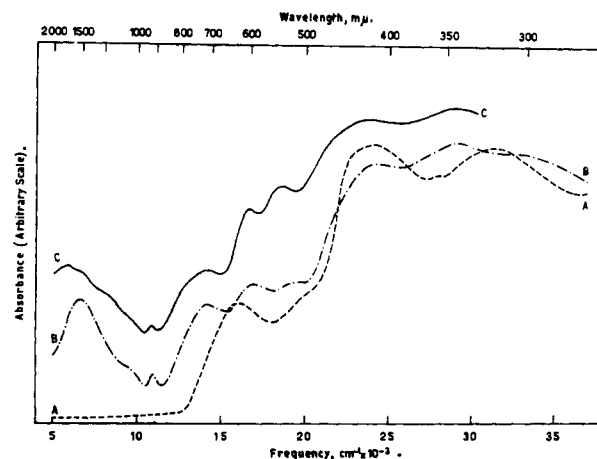


Fig. 2.—Reflectance spectra of bis-(*N*-*n*-propylsalicylaldimino)-nickel(II) (A), bis-(*N*-*i*-propylsalicylaldimino)-nickel(II) (B) and bis-(*N*-*t*-butylsalicylaldimino)-nickel(II) (C).

The spectra of these tetrahedral nickel complexes are quite similar in shape to those of the tetrahalogeno nickel(II) complexes of the type  $[\text{NiX}_4]^-$ .<sup>16</sup> On the basis of the Liehr and Ballhausen<sup>17</sup> calculations of the energy levels for tetrahedral nickel(II) complexes, and in analogy with the assignment of Goodgame, Goodgame and Cotton<sup>16</sup> for the nickel tetrahalogeno compounds, the band at 6,700  $\text{cm}^{-1}$  is assigned to the second of the three spin-allowed transitions, *i.e.*,  $\nu_2(^3T_1(F) \rightarrow ^3A_2(F))$ , and the bands at 14,100 and 16,900  $\text{cm}^{-1}$  are assigned to the highest of the three, *i.e.*,  $\nu_3(^3T_1(F) \rightarrow ^3T_1(P))$ . Due to the proximity to the charge transfer bands, it is difficult to estimate the intensity of the band at 19,600  $\text{cm}^{-1}$  and, therefore, the multiplicity of the excited state involved in the transition. In this region, however, several spin-forbidden transitions to states arising from the  $^1G$  state of the free ion are expected. The weak band at 10,900  $\text{cm}^{-1}$  is assigned as a spin-forbidden transition to an upper state arising from the  $^1D$  state of the free ion.

Bis-(*N*-*t*-butylsalicylaldimino)-nickel(II) in benzene solution at room temperature has a magnetic moment of 3.22 B.M. (Table I). This indicates that almost all of the molecules of the complex are paramagnetic ( $\mu_{\text{eff}}^{\text{solution}}/\mu_{\text{eff}}^{\text{solid}} = 3.22^2/3.3^2 = 95\%$ ). On the other hand, cryoscopic measurements of benzene solutions of this complex give a molecular weight of 431 compared to 411 for the monomeric compound (Table II). This value corresponds to only 5–10% of the complex existing as polymeric entities.<sup>18</sup> Therefore, most of the observed paramagnetism cannot be attributed to solute association but must be due to the presence of monomeric paramagnetic species. This species must have a tetrahedral structure because its spectrum in benzene solution (Fig. 3) shows the characteristic features of the reflectance spectra of tetrahedral  $\alpha$ -branched nickel(II) complexes.

Further evidence of the predominance of tetrahedral species in solutions of this complex is given by measurements of its orientation polarization,  $P_0$ . This, taken to be equal to  $P_2 = -1.2R_D$ , was found to have the value 461 cc. (Table III). This value is far greater than that for the planar *n*-alkyl complexes, which is practically zero,<sup>2</sup> approaching the value of the analogous *t*-butyl

(16) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *ibid.*, **83**, 4161 (1961); C. Furlani and G. Morpurgo, *Z. Physik. Chem.*, (Frankfurt), **23**, 93 (1961).

(17) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (New York)*, **6**, 1341 (1959).

(18) In this and following analogous calculations, the higher figure corresponds to the formation of dimers whereas the lower one is for the formation of highly polymeric species.

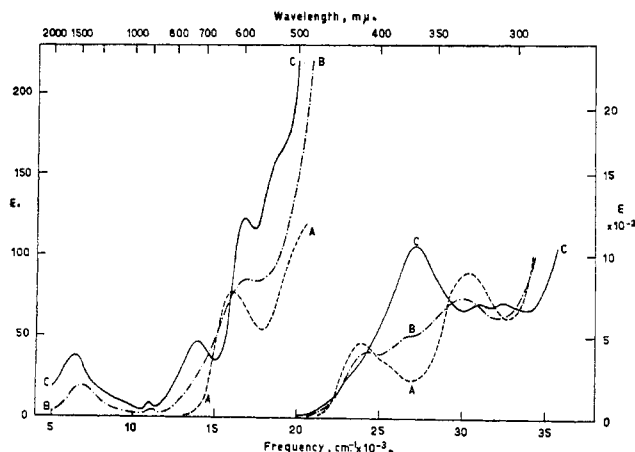


Fig. 3.—Absorption spectra of bis-(N-*n*-propylsalicylaldimino)-nickel(II) (A), bis-(N-*i*-propylsalicylaldimino)-nickel(II) (B) and bis-(N-*t*-butylsalicylaldimino)-nickel(II) (C), in benzene at 25°.

cobalt(II) derivatives which is 523 cc. The ratio of these two values provides a rough estimate of the percentage of tetrahedral forms,  $461/523 = 88\%$ .<sup>19</sup>

TABLE II

MOLECULAR WEIGHT DATA FOR BIS-(R-N-SALICYLALDIMINO)-Ni(II) COMPLEXES

R	Method	Solvent <sup>a</sup>	Concentration (g./100 g. solvent)	Mol. wt.	
				Calcd.	Found
<i>n</i> -Pr	cry	Bz	0.62–1.61	383	379 ± 9
<i>i</i> -Pr	cry	Bz	1.13–2.85		439 ± 9
	cry	Cyhx	0.50		463 ± 2
	ebf	Bz	7.80		381
<i>n</i> -Bu	cry	Bz	2.26–3.05	411	406 ± 3
<i>s</i> -Bu	cry	Bz	2.57–3.80		457 ± 7
	ebf	Bz	7.94		420
<i>t</i> -Bu	cry	Bz	3.27–4.44		431 ± 2
<i>n</i> -Hex	cry	Bz	1.26–3.01	467	469 ± 6
Cyclopent.	cry	Bz	0.88	435	650 ± 15
	ebf	Bz	6.35		461

<sup>a</sup> Bz, benzene; Cyhx, cyclohexane. The freezing point constant for benzene was taken as 51. The value of the benzene ebullioscopic constant (25.4) was obtained using bis-(N-*n*-hexylsalicylaldimino)-nickel(II) as reference substance.

TABLE III

DIELECTRIC POLARIZATION DATA FOR SOME BIS-(R-N-SALICYLALDIMINO)-M(II) COMPLEXES IN BENZENE AT 25°

M	R	R <sub>D</sub> , cc.	P <sub>90</sub> , cc.	P <sub>0</sub> , cc.	μ, D
Co	<i>i</i> -Pr	121	594	449	4.69
	<i>n</i> -Bu	130	594	438	4.62
	<i>s</i> -Bu	130	595	439	4.63
	<i>t</i> -Bu	130	679	523	5.05
Ni	<i>n</i> -Pr <sup>a</sup>	117	140	0	0.00
	<i>i</i> -Pr	117	269	129	..
	<i>n</i> -Bu <sup>a</sup>	127	149	0	0.00
	<i>s</i> -Bu	127	264	112	..
Zn	<i>t</i> -Bu	127	613	461	..
	<i>i</i> -Pr	117	679	539	5.13
	<i>n</i> -Bu	127	657	506	4.97
	<i>s</i> -Bu	127	658	507	4.98

<sup>a</sup> Cf. ref. 2.

(19) On the basis of the dielectric measurements carried out on the bis-(N-methylsalicylaldimine)-nickel(II) complex,<sup>3</sup> it must be expected that the orientation polarization value of the associated forms is very low, being almost negligible. In addition the planar species are apolar, *i.e.*, *trans*-planar. The sole form which is highly polar, therefore, is the tetrahedral one, and its dipole moment is estimated to be only a little higher than that of the analogous cobalt(II) complex.<sup>19</sup>

(20) P. J. McCarty and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 2106 (1956).

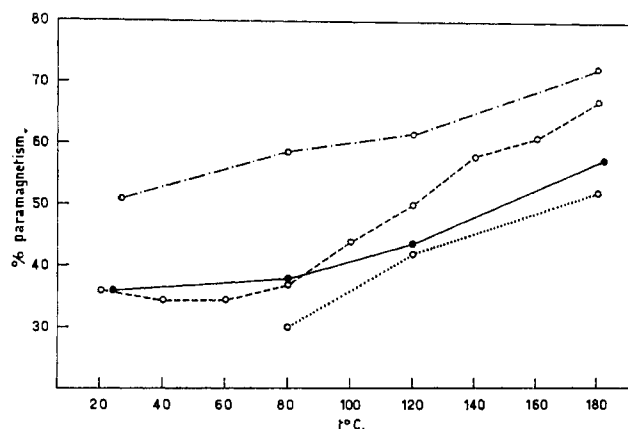


Fig. 4.—The percentages of paramagnetic forms of some  $\alpha$ -branched N-substituted salicylaldimino-nickel(II) complexes in xylene and bibenzyl solutions as a function of temperature; ---, *i*-propyl; —, *s*-butyl; ···, cyclopentyl; ····, cyclohexyl.

A benzene solution of bis-(N-*i*-propylsalicylaldimino)-nickel(II) at room temperature has a magnetic moment of 2.14 B.M., which is indicative of *ca.* 44% of high spin forms. The molecular weight found in freezing benzene, 440 as compared with 383 for the monomer, shows that only 12–25% of nickel(II) is bound in associated species. Here, too, the presence of tetrahedral forms is clearly revealed by the absorption spectrum of the *i*-propyl complex in benzene solution which shows the two characteristic bands at 6,800 and 11,200  $\text{cm}^{-1}$  (Fig. 3). These spectrophotometric data are in accordance with those reported by Holm.<sup>4</sup> In other regions of the spectrum there is a marked interference by associated and planar species. The latter presumably has a spectrum similar to that of the *n*-propyl derivative reported for comparison in Fig. 3.

By comparing the orientation polarization value for this nickel(II) complex, 129 cc., with the values for the analogous cobalt(II) and zinc(II) compounds, 449 and 539 cc., respectively (Table III), the amount of the tetrahedral forms may be estimated at about 25%. This value is in accordance with the amount of the paramagnetism not attributable to association.

The situation regarding the *s*-butyl complex is very similar. In this case, measurements of the type described above indicate that in benzene solution at room temperature there exists a conformational equilibrium containing associated (10–20%), tetrahedral (25% *ca.*) and planar species.

**Temperature Effect on the Conformational Equilibrium.**—The  $\mu_{\text{eff}}$  values of xylene and bibenzyl solutions increase with a temperature increase from 1.98 at 20° to 2.70 B.M. at 180° for the *i*-propyl and from 1.98 at 24° to 2.51 B.M. at 182° for the *s*-butyl complex (Fig. 4). Correspondingly, the percentage of paramagnetic species increases approximately from 36 to 67% and from 36 to 57%, respectively. The extent of association for the *i*-propyl and *s*-butyl complexes in benzene decreases with increase in temperature. The molecular weights found in boiling benzene are 393 and 418, respectively, which indicate not more than 5% of association at 80°.

The absorption spectrum of the *i*-propyl complex in xylene and bibenzyl from room temperature to 160° shows a progressive growth of the bands characteristic of the tetrahedral species (Fig. 5). In particular, there is a steady increase in the extinction coefficients of the  $\nu_2$  band and the one at 11,100  $\text{cm}^{-1}$ , while the shoulders of the band above 12,000  $\text{cm}^{-1}$  become more pronounced. Evidently, the percentage of tetrahedral species increases steadily with increase in temperature.

The fact that the  $\mu_{\text{eff}}$  values between room temperature and 80° are roughly constant suggests that the increase in the number of the tetrahedral paramagnetic forms, in this range of temperature, is roughly counterbalanced by a decrease in the number of associated species. At temperatures above 80°, there are practically no more associated species. This fact is reflected also in the appearance of two isosbestic points at 14,800 and 16,000  $\text{cm}^{-1}$ .

**$\alpha$ -Branched Complexes Diamagnetic in the Solid State.**—The bis-N-cyclopentyl-, bis-N-cyclohexyl and bis-(N-cyclooctylsalicylaldimino)-nickel(II) complexes are diamagnetic in the solid state (Table I). They must be considered planar and their reflectance spectra are quite similar, at least in the crystal field region, to those of the *n*-alkyl nickel(II) complexes. Furthermore, the cyclohexyl complex was found to be isostructural with the palladium(II) analog.

Magnetic susceptibility measurements of these compounds in benzene solution at room temperature by Holm,<sup>4</sup> correspond to 60 and 30%, respectively, of its being in the high spin state. For the cyclopentyl compound association may account for all of the paramagnetism. In fact cryoscopic measurements in solution of this complex confirmed the molecular weight of 650 reported by Holm,<sup>4</sup> as compared with a value of 435 for the monomer. However, the reliability of such a value is dubious because of the small freezing-point lowering obtained, 0.07° *ca.*, due to the low solubility of this compound. Furthermore, the absorption spectrum at room temperature clearly shows that tetrahedral species are also present in solution. In fact, the absorption bands at 6,800  $\text{cm}^{-1}$  ( $\epsilon_{\text{max}} = 22$ ) and at 11,100  $\text{cm}^{-1}$  ( $\epsilon_{\text{max}} = 5$ ) as well as the shoulders at about 14,000 and 17,000  $\text{cm}^{-1}$ , characteristic of a tetrahedral structure, are present.

On increasing temperature, association diminishes to 5–10% in boiling benzene (Table II). On the contrary, the magnetic moment of the solute increases from 2.36 B.M. at 27° in xylene to 2.81 B.M. at 180° in dibenzyl, which corresponds to an increase in high spin species from 50 to 70% *ca.* (Fig. 4). The percentage of tetrahedral forms, therefore, increases with increase in temperature, a fact confirmed by the steady increase up to 180° ( $\epsilon_{6,800} = 37$ ;  $\epsilon_{11,100} = 9$ ) in the bands characteristic of the tetrahedral configuration. Extinction coefficient values are almost the same as those for the *i*-propyl nickel(II) complex at the same temperature suggesting that the percentage of tetrahedral forms is roughly the same for both complexes.

The cyclohexyl and cyclooctyl compounds behave in an analogous manner. In the first case the percentage of high spin forms, as evaluated by magnetic measurements, increases from 30% at 80° in xylene to 52% at 180° in dibenzyl. The absorption spectra from 25 to 180° show a steady increase in the amount of tetrahedral forms (with the  $\nu_2$  band:  $\epsilon_{25} = 12$ ;  $\epsilon_{180} = 30$ ; with the 11,100  $\text{cm}^{-1}$  band:  $\epsilon_{25} = 3$ ,  $\epsilon_{180} = 8$ ).

**Conclusions.**—Solutions of  $\alpha$ -branched nickel(II) complexes in inert solvents contain a certain percentage of tetrahedral species. These forms are in equilibrium with a comparable amount of planar forms and (near room temperature) of associated species. Therefore, the stabilities of these forms are comparable. This is not the case with solutions of *n*-alkyl complexes which appear to contain no tetrahedral species at room temperature.<sup>2</sup>

This fact may be attributed both to steric and electronic factors. Since the crystal field stabilization energy with a given ligand is lower for a tetrahedral than for a planar structure,<sup>21</sup> the tetrahedral configura-

tion is favored by those ligands which produce a weaker crystal field. In the present case, although the inductive electron releasing effect at the nitrogen of the parent amines, as measured by the Taft  $\Sigma\sigma^*$  constant, diminishes from the normal through the secondary to the tertiary amines,<sup>22</sup> the crystal fields produced by the

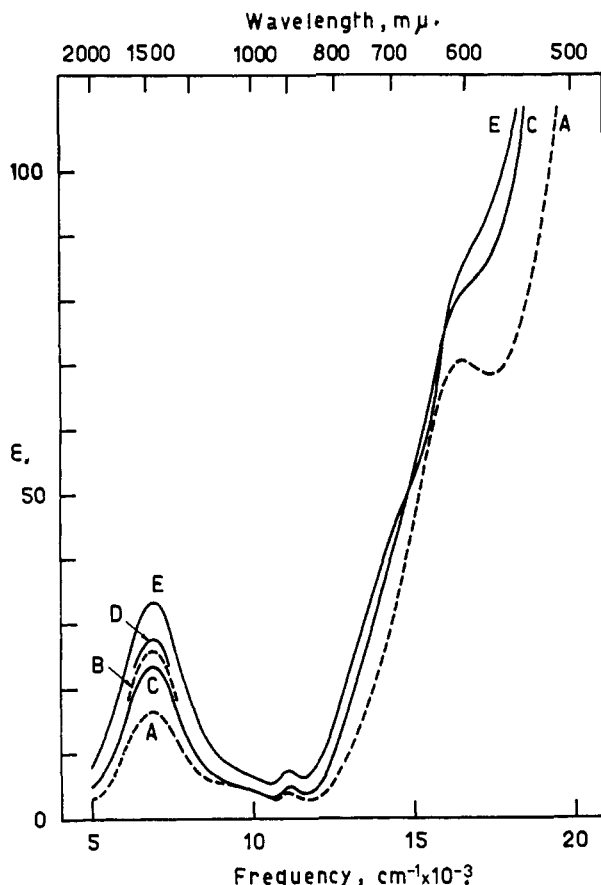


Fig. 5.—Absorption spectra of bis-(N-*i*-propylsalicylaldimino)-nickel(II) in xylene --- and bibenzyl —; (A) 20°, (B) 80°, (C) 80°, (D) 120°, (E) 160°. The curves (B) and (D) are incompletely drawn for the sake of clarity.

corresponding N-substituted salicylaldimines are practically equal. This is proved by the lack of any shift in the spectra of the tetrahedral *n*-, *s*- and *t*-butylsalicylaldimino-cobalt(II) complexes. The percentage of tetrahedral forms increases with the bulkiness of the R group, reaching its highest value for *t*-butyl, indicating that stabilization of the tetrahedral form is essentially steric in character. Furthermore, an increase in temperature favors the formation of tetrahedral species so that the enthalpy of formation is higher for these species than for the other two forms.

The two series of  $\alpha$ -branched complexes, with open and closed chain, respectively, which behave in the same way in solution, present two different structures in the solid state. Those of the first type have a tetrahedral structure whereas those of the second are planar. Evidently the difference in the steric requirements of the R group is sufficient to bring about one or the other structure.

NOTE ADDED IN PROOF.—A complete tridimensional Fourier analysis performed by M. R. Fox, E. C. Lingsfelter, P. L. Orioli and L. Sacconi has shown the bis-(N-*i*-propylsalicylaldimino)-nickel(II) complex to have a distorted tetrahedral structure.

(21) Cf. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

(22) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 3120 (1952); **75**, 4231 (1953).

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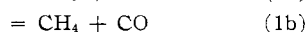
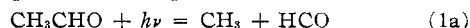
## Energy Dissipation from Excited Acetaldehyde Molecules<sup>1</sup>

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Energy dissipation in acetaldehyde vapor following absorption at various wave lengths from 2537 to 3340 Å. has been studied. At the longer wave lengths dissociation and intersystem crossover to the ground state from a triplet state account for most of the dissipation. At shorter wave lengths dissociation becomes of increasing importance. This dissociation probably occurs from high vibration levels of the singlet state but the possibility of rapid transition through a triplet state cannot be excluded. As shown previously by other authors, the mode of dissociation changes with wave length.

The photochemistry of acetaldehyde vapor has been very extensively studied.<sup>3</sup> Three different primary processes may occur with varying degrees of relative importance dependent on experimental conditions



Hydrogen is a very minor product in the wave length region under investigation and hence (1c) is almost certainly of little importance. Conclusive evidence for (1a) has been found by flash photolysis<sup>4</sup> and (1b) is proved by the use of scavengers.<sup>5</sup> Since monochromatic light was not used for flash photolysis and since scavengers affect the magnitudes of primary quantum yields to unknown extents, the relative importances of (1a) and (1b) must still be considered to be unknown. The problem in acetaldehyde is more complicated than it is in the simple ketones because even at temperatures near room temperature a radical initiated chain reaction occurs and yields are difficult to relate to primary quantum yields.

The absorption spectrum of acetaldehyde vapor has also been extensively investigated.<sup>6</sup> Absorption extends from 3484 Å. to about 2350 Å., with no definite spectroscopic evidence that any part of this region consists of a continuum. Other absorption regions at shorter wave lengths need not concern us here.

Emission from acetaldehyde also has been investigated. It extends from about 3500 to about 4800 Å.<sup>7,8</sup> A brilliant green emission is associated with the presence of biacetyl,<sup>9</sup> which is one of the photochemical reaction products.

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract AF 49(638) 679.

(2) National Institutes of Health Predoctoral Fellow 1960-1962.

(3) For reviews see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 340, and E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, pp. 284-306. The early work of P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, **55**, 1766 (1933), has been followed by several papers by Blacet and his collaborators as well as from other laboratories. References will be given in the present article only to those publications germane to the particular aspects of the photochemistry of acetaldehyde being discussed.

(4) G. Herzberg, *Proc. Chem. Soc. (London)*, 116 (1959).

(5) F. E. Blacet and D. J. Heldman, *J. Am. Chem. Soc.*, **64**, 889 (1942); F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942); A. S. Buchanan, *J. Chem. Soc.*, 2317 (1951).

(6) S. A. Schou, *J. chim. phys.*, **26**, 27 (1929); E. Eastwood and C. P. Snow, *Proc. Roy. Soc. (London)*, **A149**, 434 (1935); V. R. Rao and I. A. Rao, *Indian J. Phys.*, **28**, 491 (1954). See also P. A. Leighton and F. E. Blacet, *ref. 3*.

(7) E. Murad, *J. Phys. Chem.*, **64**, 952 (1960); Ph.D. Thesis, University of Rochester (1959).

(8) P. Longin, *Compt. rend.*, **251**, 2499 (1960).

(9) M. S. Matheson and J. W. Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

While light emission in this instance is a minor means of energy dissipation, the existence of an emission often leads to useful conclusions concerning the fates of various excited states of absorbing molecules. The present work was undertaken to attempt to assess the roles of singlet and triplet states of acetaldehyde in its photochemistry. Toward the long wave length end of the absorption region both singlet and triplet emission occur. The use of nitric oxide as a scavenger permits some conclusions to be drawn but since it quenches triplet emission it may also have an effect on the magnitude of any primary dissociation which may arise from that state. Further work on primary quantum yields is badly needed but this would be of little value unless proper methods for such studies can be developed.

## Experimental

Eastman Grade acetaldehyde, Eastman Grade biacetyl, and Eastman Spectro Grade acetone were degassed and distilled bulb-to-bulb in a grease-free high vacuum system. The middle third was retained for use in each case. Analysis by vapor-phase chromatography showed the acetaldehyde and the biacetyl to be about 99.7% pure. No impurities could be detected in the acetone by a similar analysis.

The impurity in acetaldehyde had no effect on acetaldehyde emission. This was determined by observing emission from acetaldehyde specially purified by collection from a vapor-phase fractometer.

Matheson nitric oxide was purified by repeated vacuum distillation from a bulb at -159° to a bulb at -195°. No impurities were detectable by mass spectrometric analysis. Airco Reagent Grade oxygen and Phillips Research Grade methane were used without further purification.

A conventional glass high vacuum apparatus free from stop-cock grease was used for all experiments. The quartz cell was T-shaped, with each of its three windows 22 mm. in diameter. The area of the exciting radiation incident on the cell window was limited by a 14 mm. diameter diaphragm to about 1.56 cm.<sup>2</sup>. This diaphragm reduced reflection of incident radiation from the walls of the cell. The path length of the incident light beam in the cell was 56 mm. The volume of the cell section (including a magnetically operated stirrer and connecting tubing) was about 190 ml. The cell was encased in an electrically heated aluminum block furnace.

An Osram HBO-500W high pressure mercury arc lamp was used for all emission experiments and for all photolysis experiments at wave lengths other than 2537 Å. A Hanovia S-100 mercury arc lamp was used for photolysis experiments at 2537 Å. The desired wave lengths were isolated from these sources by a Bausch and Lomb Grating Monochromator with a linear dispersion of 33 Å., per mm. Light from the monochromator was collimated and after passage through the cell was focused on an RCA 935 phototube by quartz lenses.

With the monochromator slit widths generally used in these experiments, the total radiation in the incident beam in the cell from the Osram lamp (expressed in photons per ml. per second) was about  $5 \times 10^{14}$  at 3340 Å., about  $1 \times 10^{14}$  at 3130 Å., about  $5 \times 10^{13}$  at 2967 Å., and about  $1 \times 10^{13}$  at 2804 Å. The intensity at 2537 Å. from the Hanovia S-100 lamp was about  $1 \times 10^{12}$  quanta per ml. per second. These calculations are based on a light beam volume of 9.74 ml.