and HfC and the pattern of rhenium metal. However, it is possible that the product of the reaction could alternatively be a solution of rhenium in the ZrC and HfC. The lattice constant calculated for the cubic phase was a_0 = 4.668 Å. for the product of the $ZrRe_2$–C reaction and a_0 = 4.616 Å. for the product of the $HfRe_2$–C reaction.[8]

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(8) Material supplementary to this article has been deposited as Document Number 6323 with the ADI Auxiliary Publications Project Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $2.50 for photoprints, or $1.75 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

INFRARED AND ULTRAVIOLET ABSORPTION SPECTRA OF SOME SALTS AND METAL CHELATES OF ANTHRANILIC ACID

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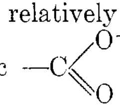
Absorption maxima in the 3000 and 1550 cm.$^{-1}$ regions in potassium bromide disks, and in the 300 mμ region in potassium bromide disks and in ethanol solutions are reported for anthranilic acid, its sodium, potassium, calcium, stontium and barium salts and its chelates with magnesium, zinc, cadmium, nickel and copper. Chelation shifts the 320 mμ band of the anthranilate ion to shorter wave lengths, decreases the frequencies of the N—H stretching vibrations, causes an inversion of the relative intensities of the 1615 and 1580 cm.$^{-1}$ peaks and effects small shifts to higher frequencies of the band attributed to the antisymmetric COO^- stretching vibration. The spectra indicate a *trans* planar square configuration for all complexes. The chelates are appreciably dissociated in ethanol.

The usual effect of chelation of organic ligands with metals is to shift the ultraviolet absorption maxima of the ligands to longer wave lengths. Sone[2] has reported an extensive study of this effect and has concluded that for some complexes the extent of this shift is related to the strength of the ligand-to-metal bonds. It appeared to the authors that the direction of this shift might be reversed in metal chelates having as one of the donor centers an aryl amino group, as the formation of the fourth bond by the nitrogen atom results in a blocking of resonance between the amino group and the benzene ring. Hypsochromic shifts in the long wave length absorption maximum of N,N-dimethylaniline have been observed on coördination of this amine with sulfur trioxide[3] and with boron trichloride.[4]

The anthranilate (*o*-aminobenzoate) ion was selected for this investigation. The complexes studied were those of magnesium, zinc, cadmium, nickel and copper. As the cations of the first three metals do not absorb in the near ultraviolet, any changes in the absorption pattern of the anthranilate ion on chelation are most probably associated with changes in the absorption characteristics of the ligand itself. The spectra of sodium, potassium, calcium, strontium and barium anthranilates were obtained for comparison with those of the chelates.

The infrared spectra of these compounds were also determined in an effort to obtain information regarding the type of bonding between the ligand and the metal ions, as well as the configuration of the complexes. The spectra of the 2:1 complexes of aliphatic amino acids with copper and nickel[5] reveal decreases in the frequencies of the N–H stretching vibrations, indicating covalent N–M bonds, and a relatively small perturbation of the antisymmetric



$-C{\overset{O^-}{\underset{O}{\lessdot}}}$

stretching vibration, suggesting essentially electrostatic COO^----M^{++} bonds. These data, together with the X-ray evidence for a *trans* coplanar square configuration of nickel and copper complexes of amino acids[6] and the magnitudes of their magnetic moments, were interpreted[5] as indicating the use of sp linear bond orbitals by copper and nickel in forming nitrogen-to-metal bonds. This interpretation was also applied to the spectrum of bis-(glycino)-zinc monohydrate[7] and recent X-ray evidence[8] has revealed a *trans* coplanar square arrangement of the nitrogen atom and an oxygen atom of each carboxylate group about the metal in the monohydrates of bis-(glycino)-zinc and bis-(glycino)-cadmium, with the metal atoms bound also by apparently longer

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[1] Sister Ann Gertrude Hill, O.S.U., Ursuline College, Cleveland, Ohio. Supported under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame.

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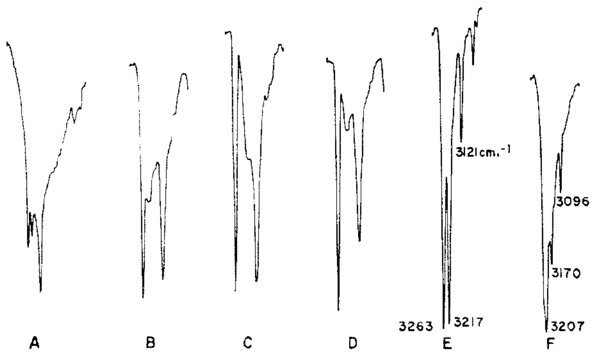

Fig. 1.—Absorption patterns in the 3000 cm.$^{-1}$ region in KBr disks: A, sodium anthranilate; B, bis-(anthranilato)-copper(II); C, bis-(anthranilato)-magnesium; D, bis-(anthranilato)-zinc; E, bis-(aniline)-dichlorozinc; F, *o*-phenylenediaminedichlorozinc.

bonds to carboxylate oxygen atoms directly above and below the metal atoms.

It is of interest to determine whether the structures characteristics of the aliphatic amino acids extend also to the metal chelates of aromatic amino acids, for which no X-ray data are available. Of particular interest are the zinc and cadmium chelates, as the great majority of compounds of these metals have a tetrahedral configuration due to the use of sp^3 bond orbitals.

Experimental

Anthranilic acid, Eastman material, was purified by vacuum sublimation or by recrystallization from hot water using a small amount of decolorizing charcoal.

Sodium and potassium anthranilates were prepared by mixing ethanol solutions of sodium or potassium hydroxide and anthranilic acid.

Sodium anthranilate solution was prepared by dissolving anthranilic acid in an equivalent amount of aqueous 1 *N* sodium hydroxide. After filtration, small quantities of the acid were added until the solution was very weakly acid. A freshly prepared solution was used for each preparation.

Bis-(anthranilato) complexes of magnesium, zinc, cadmium, nickel and copper were prepared by addition of aqueous solutions of the metal chlorides to a solution of sodium anthranilate. The precipitates were washed with several portions of distilled water and ethanol and vacuum dried at 130°.

Anal. Calcd. for Mg($C_7H_6O_2N_2$): $C_7H_6O_2N$, 92.48. Found: $C_7H_6O_2N$, 92.4. Calcd. for Zn$(A)_2$: C, 49.80; H, 3.58; N, 8.28; Zn, 19.36. Found: C, 50.1; H, 3.78; N, 8.9; Zn, 19.3. Calcd. for Cd$(A)_2$: Cd, 29.22. Found: Cd, 29.35. Calcd for Ni$(A)_2$: C, 50.84; H, 3.65; N, 8.47. Found: C, 50.42; H, 3.91; N, 8.93. Calcd. for Cu$(A)_2$: Cu, 18.82. Found: Cu, 18.8.

Calcium, strontium and barium anthranilates were prepared by heating solutions of the chlorides of these metals in distilled water to 80° and adding with stirring to a sodium anthranilate solution. The white crystalline products were washed with a dilute solution of sodium anthranilate and finally with ethanol. The compounds were vacuum dried at 120°.

Anal. Calcd. for Ca($C_7H_6O_2N)_2$: $C_7H_7O_2N$, 87.88. Found: $C_7H_7O_2N$, 88.2. Calcd. for SrA$_2$: $C_7H_7O_2N$, 76.26. Found: $C_7H_7O_2N$, 77.1. Calcd. for BaA$_2$: $C_7H_7O_2N$, 66.95. Found: $C_7H_7O_2N$, 66.3.

Absorption measurements in the ultraviolet region were obtained with a Beckman DU spectrophotometer equipped with a Warren Spectracord attachment. Infrared spectra were obtained with a Perkin–Elmer Model 21 instrument, using a sodium chloride or calcium fluoride prism. The concentration of the KBr disks used for infrared measurements was about 0.5 mg. of sample in 300 mg. of KBr. In preparing the disk of anthranilic acid hydrochloride the die was not evacuated.

Results and Discussion

It has been demonstrated previously[9] that the coördination of amino groups with metals (the formation of nitrogen-to-metal dative bonds) results in appreciable decreases in the frequencies of the N–H stretching vibrations. The absorption maxima in the 3000 cm.$^{-1}$ region listed in Table I reveal that the compounds studied fall into two classes: sodium, potassium, calcium, strontium and barium salts, and magnesium, zinc cadmium, nickel and copper complexes. The high frequency peaks in the spectra of the former compounds are close to the value for anthranilic acid, whereas the spectra of the latter compounds reveal shifts of 149–187 cm.$^{-1}$ to lower frequencies. The cupric ion is expected to form the strongest N–M bond and the greatest shift is observed in the spectrum of the copper complex. The shifts are greater than those observed in this Laboratory in the spectra of metal complexes of aliphatic amino acids.

The absorption profiles in the 3000 cm.$^{-1}$ region are determined by the strength of coupling between the amino groups, their relative conformations and the extent of hydrogen bonding. The similarities between the absorption patterns in this region for the magnesium, zinc, cadmium, nickel and copper complexes suggest to the authors that they all have similar configurations. A comparison, Fig. 1, of these patterns with those of bis-(aniline)-dichlorozinc and *o*-phenylenediaminedichlorozinc, patterns typical of tetrahedral zinc complexes, suggests that the anthranilate complexes have a *trans* square planar arrangement of the four coördinating atoms about the metal atom. This is expected for the copper and nickel complexes and is not surprising for the others in view of the X-ray evidence for the glycino chelates. All the complexes except that of copper have almost identical spectral in the 2–15 μ region, and the spectrum of the copper complex differs significantly from the others only in the 1050 cm.$^{-1}$ region. The nickel chelate is paramagnetic, having a moment of 3.2 magnetons.[10] This is a typical value for an outer orbital complex of nickel(II) having an octahedral or tetragonal configuration. Tetrahedral complexes of nickel-(II) are expected to have a larger orbital contribution to the magnetic moment; values of 3.6–4.0 have been reported recently for such complexes.[11]

The spectra of the anthranilates in the 1625–1520 cm.$^{-1}$ region reveal three absorption peaks that are not changed appreciably on deuteration of the amino group. The two high frequency peaks at 1615 and 1582 cm.$^{-1}$ in the salts are attributed to C=C ring vibrations and the third, the strongest in the spectra of all but the magnesium complex, is attributed to the antisymmetric COO$^-$ stretching vibration (with perhaps some contribution from a third ring vibration). Stimson[12] has also assigned this peak in the spectra of the sodium and potassium salt to the COO$^-$ vibration, and a similar as-

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TABLE I

ABSORPTION MAXIMA OF ANTHRANILIC ACID, ITS HYDROCHLORIDE, SALTS AND CHELATES IN KBr DISKS

	Ultra-violet, mμ	3500–3100 cm.$^{-1}$ cm.$^{-1}$ (%T)			1625–1500 cm.$^{-1}$ cm.$^{-1}$ (%T)		
Acid	335	3460(26)	3367(29)				1670(6)
Acid·HCl	282						1695(9)
Salts							
Na	312	3436(44)	3400(47)	3330(35)	1615(18)	1580(30)	1521(9)
K	318	3420(39)	3280(37)		1614(7)	1583(11)	1520(6)
Ca	323	3472(59)	3424(59)	3344(49)	1615(11)	1580(20)	1521(9)
Sr	320	3428(44)	3367(51)	3303(51)	1615(9)	1585(16)	1520(5)
Ba	319	3436(27)	3389(34)	3311(37)	1617(36)	1583(41)	1519(11)
Chelates							
Mg	294	3311(29)	3202(57)	3145(38)	1623(10)	1605(6)	1564(8)
Zn	296	3294(30)	3222(59)	3130(35)	1620(20)	1596(10)	1545(5)
Cd	298	3289(40)	3257(55)	3140(53)	1619(20)	1590(7)	1534(4)
Ni	289	3303(53)	3215(74)	3120(65)	1623(27)	1609(18)	1550(7)
Cu	284	3273(35)	3230(53)	3125(38)	1616(18)	1594(6)	1540(4)

signment of the peak at 1554 cm.$^{-1}$ in the spectrum of sodium benzoate has been made by Davies and Jones.[13]

The data in Table I reveal an inversion of the relative strengths of the absorption peaks at 1615 and 1582 cm.$^{-1}$ on chelation; the higher frequency peak is stronger in the salts and weaker in the chelates. The peak at 1582 cm.$^{-1}$ in the salts is shifted an average of 17 cm.$^{-1}$ to higher frequency on chelation. The shifts in the 1520 cm.$^{-1}$ peak on chelation are 14, 20, 25, 30 and 44 cm.$^{-1}$ for the cadmium, copper, zinc, nickel and magnesium complexes, respectively. In the spectra of the acid, acid chloride and methyl ester the carbonyl peaks occur at 1670, 1695 and 1697 cm.$^{-1}$, respectively. A comparison of the small shifts observed on chelation to the very large shifts on acid and ester formation suggests to the authors that in the anthranilato complexes the COO^{-}---M^{++} bonds are essentially electrostatic.

If the chelates have a *trans* planar configuration, as interpreted from the spectra, it may well be that the complexes in adjacent planes in the crystal lattice are so arranged as to permit octahedral coördination by carboxylate oxygen atoms directly above and below the metal atoms, as observed[8] in the monohydrates of bis-(glycino)-zinc and bis-(glycino)-cadmium. This arrangement is expected particularly for bis-(anthranilato)-nickel. If this octahedral coördination prevails, the bonds may have some sp^3d^2 character, but it appears to the authors that they are essentially sp N–M bonds and electrostatic O---M bonds. Intermolecular O---H–N hydrogen bonds are expected for these complexes in the solid state. For such interaction the N–H stretching peaks are surprisingly sharp, as they are in the spectrum of *trans*-bis-(glycino)-platinum(II),[14] for which a similar configuration and somewhat similar hydrogen bonding are probable.

The long wave length absorption maxima in the ultraviolet region for anthranilic acid, its hydrochloride, salts and metal chelates in potassium bromide disks are listed in the first column of Table I. The decrease in λ_{max} from the acid to the salts is associated with the weaker electron withdrawing character of the COO^- group compared to that of the COOH group. The further decrease on chelation is attributed to the blocking of resonance between the amino group and the ring by the formation of N–M bonds. The hydrochloride spectrum shows the greatest shift, followed by that of the copper chelate; with the exception of the magnesium chelate, the shifts are in the accepted order of nitrogen-to-metal bond strengths. These hypsochromic shifts are, of course, not so large as those observed on the chelation with metals of such highly conjugated ligands as Eriochromeschwarz T[15] and the purpurate anion,[16] in which chelation constrains the flow of π-electrons.

The spectra of anthranilic acid in potassium bromide and ethanol differ in that the 247 mμ peak in ethanol is a shoulder in the disk. A point of inflection occurs at 243 mμ in KBr and it is not shifted appreciably on salt formation or in the cadmium and zinc chelates. Ultraviolet spectra were also obtained in absolute ethanol and 95% ethanol for the compounds listed in Table I. The low solubilities of the zinc, cadmium, nickel and copper chelates necessitated the use of 10 cm. cells for the spectra of these complexes. The spectrum of the magnesium complex in absolute ethanol resembles very closely the curves for the calcium, strontium and barium salts, indicating that practically all the nitrogen-to-magnesium bonds are broken in solution; the ligand is probably displaced by alcohol molecules, an indication of the preference of magnesium for O–M bonds. This solvation of the magnesium cation is further evidenced by the greater solubility of the magnesium complex in ethanol compared to the other chelates. The spectra reveal that a portion of the bonds joining nitrogen to zinc, cadmium and copper are broken in absolute ethanol, and that in 95% ethanol the

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nickel chelate is completely dissociated and the copper, zinc and cadmium chelates are appreciably hydrolyzed.

The dissociation of these chelates in solutions of high dielectric constant is attributed to the electrostatic character of the COO^{-}—M^{++} bonds and to the gain in resonance stabilization on the rupture of the nitrogen-to-metal bonds. It is evident that the study of the effect of chelation on weak ligands such as the anthranilate ion necessitates the determination of the spectra of the chelates in the solid state.

THE REACTION BETWEEN OXYGEN ATOMS AND DIBORANE[1,2]

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The gas-phase reaction between diborane and oxygen atoms, produced by the mercury photosensitized decomposition of nitrous oxide, has been studied at 25 and 100°. The only products formed initially are N_2 (internal actinometer), H_2, B_4H_{10}, B_5H_9 and a white solid with the empirical formula BHO. Observed initial rates compare favorably with those predicted from mechanism 2–7. A steady-state tetraborane concentration is reached at low diborane decomposition, due to the faster competitive reaction $O + B_4H_{10} \rightarrow BH_3O + B_3H_7$.

Introduction

The reaction between molecular oxygen and diborane has been studied at the explosion limits by several investigators.[3-5] Roth and Bauer[5] have proposed the following mechanism at the second explosion limit

$$B_2H_6 \rightleftarrows 2BH_3$$
$$BH_3 + O_2 \longrightarrow BH_2OH + O$$
$$O + B_2H_6 \longrightarrow BH_2OH + BH_3$$
$$BH_2OH + B_2H_6 \longrightarrow BH_3 + B_2H_5OH$$
$$BH_3 + O_2 + M \longrightarrow HBO_2 + H_2 + M$$
$$BH_3 + B_2H_6 \longrightarrow B_3H_7 + H_2$$
$$B_3H_7 \longrightarrow \text{higher hydrides}$$
$$(B_2H_5OH \text{ disproportionates to } B(OH)_3 + B_2H_6)$$

In addition to the explosion limit results, this mechanism has been supported by work with various diluent gases, such as N_2, He, Ar, H_2, NO, NO_2 and $Fe(CO)_5$.[6,7]

An earlier investigation[8] of the oxygen atom-diborane reaction, using oxygen atoms from a silent glow discharge in molecular oxygen, gave an activation energy of equal to, or less than, 4 kcal./mole, but the kinetic scheme was obscured by the presence of molecular oxygen and ozone.

To eliminate these competing reactions, the technique developed by Cvetanovic[9] to study the interaction of oxygen atoms with hydrocarbons was used in this work. By this method, atomic oxygen is obtained from the mercury photosensitized (using 2537 Å. light) decomposition of nitrous oxide

$$Hg(6^1S_0) + h\nu \xrightarrow{2537\ \text{Å.}} Hg(6^3P_1)$$
$$Hg(6^3P_1) + N_2O \longrightarrow N_2 + O + Hg(6^1S_0)$$

Cvetanovic found that if only nitrous oxide and mercury were present in the mixture, molecular oxygen and oxides of mercury were formed.[9] If a hydrocarbon was added, however, the sole fate of the atomic oxygen was reaction with the hydrocarbon.[10] Direct mercury photosensitized decomposition of the hydrocarbon was kept to a minimum by the use of a large excess of nitrous oxide.

Experimental

Reaction System.—The glass reaction system (total volume = 350 ml.) consisted of a closed loop for circulation of the reactants through the quartz photolysis cell. The cell was 100 mm. long and 50 mm. o.d., and was completely enclosed by an air furnace. Both the inlet and outlet of the cell were attached to traps to thermostat the excess liquid mercury. Circulation of the reaction mixture through the cell at a rate of approximately 60 ml./min. (with a pressure of 215 mm.) was achieved by means of an all-glass pump similar to that described by Dodd and Robinson.[11] The primary modification of this pump was the use of nitrous oxide (dried by passage through a $Mg(ClO_4)_2$ drying tube), rather than air, bubbling through the mercury to produce the pumping action. The relatively small amount of mechanical carryover of N_2O to the reaction system had negligible effect on the total pressure, whereas preliminary results with air or undried N_2O led to very irreproducible results in nitrogen production and diborane decomposition.

The low-pressure mercury arc was constructed of 8 mm. o.d. Vycor tubing close-wound in the form of a flat spiral three inches in diameter. It was filled with neon (12 mm.) and a drop of mercury to saturate the gas with mercury vapor. A Corning No. 7910 Vycor filter was used to eliminate light of 1849 Å. wave length from the reaction cell. The effective intensity of the 2537 Å. radiation was determined with a propane actinometer,[12] and the light was monitored with an RCA 935 photocell.

Reagents.—Diborane was prepared and purified *in vacuo* from lithium aluminum hydride and boron trifluoride etherate by the method of Shapiro, *et al.*,[13] and stored at room

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(1) From the thesis by F. P. Fehlner, submitted in partial fulfillment of the requirements for the Ph.D. degree to the Graduate School, Rensselaer Polytechnic Institute, 1959. Available from University Microfilms, Ann Arbor, Michigan.

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