Silver Ion Complexes with 2-Thenylamine and 2-Furfurylamine[1]

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The ability of 2-thenylamine and 2-furfurylamine to form complexes with metal ions has been investigated in an effort to establish whether or not the sulfur and oxygen atoms are active in coördination in these compounds.

Experimental

2-Thenylamine furnished by the Socony-Vacuum Oil Company was purified by distillation under nitrogen from barium oxide through a column packed with glass helices. The neutralization equivalent of the colorless fraction boiling at 78.5° (15 mm.) indicated a purity of 98.6%.

2-Furfurylamine furnished by the Quaker Oats Company and benzylamine purchased from Eastman Kodak Company were purified similarly by distillation from potassium hydroxide. The 2-furfurylamine boiled at 142.5–143° (735 mm.) and the benzylamine at 178° (742 mm.). The neutralization equivalents indicated purities of 99.9 and 99.7%, respectively.

Details of the experimental procedure are the same as those previously described.[2]

The terms used here and the method of calculation of constants are those given by Carlson, McReynolds and Verhoek.[3] The following constants were calculated.

FORMATION CONSTANTS OF SILVER–AMMINES

Amine	log K_{AH}	log K_1	log K_2	log $K_{Av.}$
Benzylamine	9.46	3.02	3.78	3.40
2-Thenylamine	8.92	2.87	3.64	3.26
2-Furfurylamine	8.89	2.64	3.34	2.99

Since with all three amines $\bar{n}$ approaches a limiting value of two, it is evident that the S and O atom in 2-thenylamine and 2-furfurylamine, respectively, do not coördinate with silver ion which has a characteristic coördination number of two. The ions Cu^{++}, Ni^{++}, Co^{++} and Zn^{++} gave precipitates of hydroxides before there was any evidence of complex formation. Mercury(II) ion similarly gave a white precipitate containing organic material but with no well-defined stoichiometry.

2-Thenylamine and 2-furfurylamine resemble ammonia[4] and other amines[5] in the formation of silver ion complexes in that $\log K_1 < \log K_2$. Bruehlman and Verhoek[5] found that there was a direct proportionality between $\log K_1$ and pK_{AH} for the complexes of silver ion with primary amines, including benzylamine. 2-Thenylamine and 2-furfurylamine may now be included in this generalization.

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[1] Abstracted from a portion of a thesis presented by Ely Gonick in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1951.

[2] E. Gonick, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **76**, 4671 (1954).

[3] C. A. Carlson, J. P. McReynolds and F. H. Verhoek, *ibid.*, **67**, 1334 (1945).

[4] J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[5] R. V. Bruehlman and F. H. Verhoek, THIS JOURNAL, **70**, 1401 (1948).

Zirconium (and Hafnium) Tetrachloride·Diethyl Phthalate[1]

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Addition compounds of zirconium tetrachloride and hafnium tetrachloride with esters of benzoic acid have been described in previous communications. The preparation and properties of addition compounds of the two tetrachlorides with an ester of phthalic acid are described in this paper.

Experimental

The Preparation of Addition Compounds.—The apparatus used has been described in a previous paper.[2] The same precautions must be taken to ensure anhydrous conditions. Five to 10 grams of metal tetrachloride is loaded into the reaction flask while in the dry-box. The apparatus is removed from the dry-box and 250 to 350 ml. of dry, liquid sulfur dioxide is condensed into the flask, entering through the side arm in a dropping funnel and refluxed from a Dry Ice–acetone cold finger. Diethyl phthalate is added from the dropping funnel. The solution clears abruptly when one mole of ester per mole of metal tetrachloride has been added. The solution is filtered into an identical flask through a filter stick under the vapor pressure of the solvent. The solution is allowed to evaporate to a volume of 25–50 ml. Some crystallization is noted usually at this point. Fifty to 75 ml. of cold benzene is added from a dropping funnel, which dissolves any crystalline material. A trapped aspirator pump is connected to the flask through a side arm on the dropping funnel, and the flask is evacuated. The flask is cooled externally while the pumping continues until the contents are frozen solid. Pumping is continued for 30 minutes to remove sulfur dioxide. When the flask is returned to atmospheric pressure and allowed to warm up, the white crystalline addition compound is slightly soluble in the benzene. The solvent is removed by suction through a filter stick and the product is washed with two 50-ml. portions of benzene, each of which is added through the dropping funnel and removed through the filter stick. The flask is left under vacuum overnight to remove the last traces of benzene. After the flask is placed in the dry-box the product is removed. No differences are observed between the zirconium and hafnium preparations. Yields from 75 to 80% are obtained. It is believed that the solubility of the product in benzene is the only reason for obtaining less than 100% yields. The solubility is much greater in benzene which contains sulfur dioxide.

Analysis.—The compounds were sampled in a dry-box and analyzed by standard gravimetric procedures for zirconium and hafnium and chloride. Molecular weights were determined in nitrobenzene by the freezing point lowering method using a Beckmann thermometer. In the zirconium compounds, Hf/Zr = 0.025 by weight. In the hafnium compounds, Zr/Hf = 0.022 by weight. Calcd. for $ZrCl_4 \cdot C_6H_4(COOC_2H_5)_2$: Zr, 20.23; Cl, 31.08; mol. wt., 456. Found: Zr, 20.7; Cl, 31.5; mol. wt., 471. Calcd. for $HfCl_4 \cdot C_6H_4(COOC_2H_5)_2$: Hf, 32.47; Cl, 26.31; mol. wt., 539. Found: Hf, 33.2; Cl, 25.6; mol. wt., 610.

Chemical Properties.—The addition compounds are white, freely flowing crystalline substances. They are stable in dry air. When added to water the compounds decompose, with the metal halide dissolving in the water and the ester separating as an oil. No melting points are observed for the compounds. They decompose on heating, although while decomposing they go through a liquid stage.

Thermochemical Data.—All heat measurements were made in the apparatus described previously.[2] The heats of solution of diethyl phthalate and the hafnium addition compound in nitrobenzene are too small to measure with the apparatus used. A plot of the integral heat of solution of the zirconium addition compound in nitrobenzene against the concentration from 0.025 to 0.112 molal gives a line that is slightly concave, but does not deviate too much from a straight line. The molal heat of solution at 0.1 molal dilution is 2.3 kcal./mole. Bulbs of anhydrous metal halide

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[1] From the doctoral dissertation of R. V. Moore.

[2] W. S. Hummers, S. Y. Tyree and S. Yolles, THIS JOURNAL, **74**, 139 (1952).