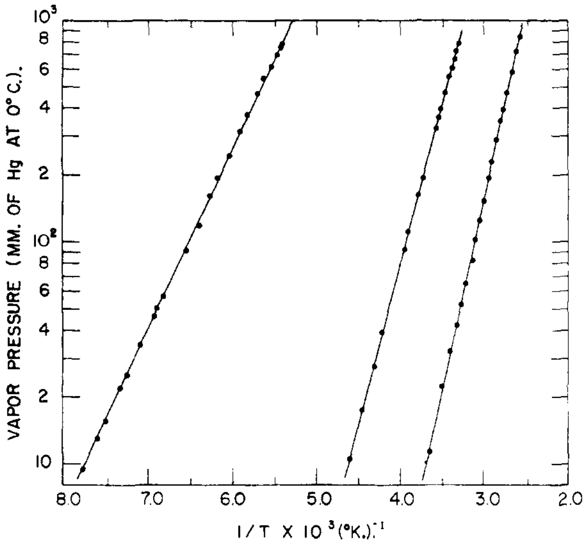

Fig. 1.

analyses showed that the deuterium isotope abundance was 99.58%.

Determination of Properties.—Low temperature measurements of vapor pressure were made using a cryostat with a constant liquid level device for the liquid nitrogen coolant. The cryostat was constructed according to details given by Scott and Brickwedde.[5] Temperature was controlled by maintaining the desired potential across a platinum resistance thermometer located inside the cryostat bath. When the temperature decreased, the resistance of the platinum thermometer also decreased and, therefore, the voltage across it was lowered. A 0–100 millivolt Brown Self-Balancing Electronik Strip Chart Recorder regulated heaters which controlled the temperature ±0.1°. The cryostat liquid bath was propane below −145° and Freon 12 or $CHCl_3$ above this temperature. Pressure was measured by means of an absolute mercury manometer, and all manometric pressures were corrected to 0° at sea level and 45° latitude. Measurements were carried out in a laboratory thermostated at 22°.

For temperatures 0° and above, either a bath of water or mineral oil was used and maintained at a constant temperature ±0.1°. The sample whose vapor pressure was being determined above 0° was sealed off in a tensiometer of the type described by Dennis, *et al.*[2] All temperatures were measured with a copper–constantan thermocouple which had been carefully standardized[6] at the following fixed points: oxygen boiling point, carbon dioxide sublimation point, and the freezing and boiling points of water.

Each vapor pressure plot is constructed from at least 20 individual measurements made between 10 mm. and 800 mm. pressure with results checked at selected points on separate samples. The data have been fitted by the least squares method to the equation

$$\log_{10} p = \frac{-\Delta H}{2.303RT} + B$$

where R = 1.987 calories per °C. per gram mole and ΔH is the latent heat of vaporization in calories per gram mole. The constants of this equation have been presented along with the other physical properties in Table I. From these equations the boiling points have been calculated.

Vapor densities were measured at room temperature and were found within experimental error to agree with the calculated values for GeD_4, Ge_2D_6 and Ge_3D_8 in which the deuterium isotopic abundance is 99.58%.

Melting points were measured using the drop ring method employed by Dennis, *et al.*[2] Triplicate determinations agreed within 0.2°.

Liquid density measurements were made as close to the melting point as was feasible because of the large temperature coefficient of expansion.

Acknowledgment.—The authors would like to express their gratitude to Don Carlson for constructing the electronic equipment. We are also indebted to Fred Schonfeld, who prepared the Mg_2Ge alloy, and to Patricia Fain, who ran the hydrogen isotopic analyses.

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[5] R. B. Scott and F. G. Brickwedde, *Bureau of Standards J. Res.*, **6**, 401 (1931).

[6] Reference 4, p. 212.

The Chemistry of Thorium. VI.[1] Some Observations on the 5,7-Dihalo-8-quinolinol Chelates of Thorium

BY THERALD MOELLER AND M. VENKATA RAMANIAH

RECEIVED DECEMBER 21, 1953

In a previous communication,[1] it was pointed out that although the two thorium chelates with 8-quinolinol, $Th(C_9H_6NO)_4$ and $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$, differ from each other in the solid state, they give absorption spectra differing only in intensities when dissolved in a variety of organic solvents. These data have been interpreted as indicating that the extra mole of 8-quinolinol in the 1 to 5 chelate is held by lattice forces. It has been of interest to extend these studies to the thorium chelates of several 5,7-dihalo-8-quinolinols. This extension has been prompted by desires to study other series of 8-quinolinol type addition compounds, previously limited to the simple 8-quinolinol derivatives of thorium,[1,2] uranium(VI),[2] plutonium(VI),[3] and scandium,[4] and to determine whether enhanced hydrolytic stabilities of the compound type in question could be achieved. Choice of 5,7-dihalo-8-quinolinols stemmed from an earlier observation of improvements in stabilities and extractabilities of tripositive rare earth metal chelates through use of the 5,7-dichloro material.[5] The investigation involved study of conditions for preparation of both 1 to 4 and 1 to 5 type chelates and measurements of absorption spectra in organic solvents.

Experimental

Materials Used.—The source of thorium ion was a sample of thorium nitrate 4-hydrate, obtained from the Lindsay Chemical Company and shown to be free from yttrium and the rare earth elements. Halogen substituted 8-quinolinols were reagent quality materials supplied by the Eastman Kodak Co. and the Matheson Co. They were recrystallized from acetone and ethanol prior to use. Reagent quality chloroform (containing *ca.* 1% ethanol by volume) and ethanol were used without treatment except as specified otherwise.

Thorium nitrate solutions were standardized gravimetrically by weighing as the oxide. The substituted 8-quinolinols were used as acetone solutions containing 3 g. of reagent per liter of solvent.

Apparatus.—All absorption spectra were measured at *ca.* 25° with a Cary Recording Spectrophotometer, using 5.0 cm. demountable cells with quartz windows. All *p*H measurements were made with a Beckman model G *p*H meter.

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[1] For the preceding communication in this series, see T. Moeller and M. V. Ramaniah, THIS JOURNAL, **75**, 3946 (1953).

[2] F. J. Frere, *ibid.*, **55**, 4362 (1933).

[3] B. G. Harvey, H. G. Heal, A. G. Maddock and E. L. Rawley, *J. Chem. Soc.*, 1010 (1947).

[4] L. Pokras and P. M. Bernays, THIS JOURNAL, **73**, 7 (1951).

[5] T. Moeller and D. E. Jackson, *Anal. Chem.*, **22**, 1393 (1950).

Preparation of Substituted 8-Quinolinol Chelates.—Preliminary experiments showed that although the 5,7-dihalo-8-quinolinols studied yielded both 1 to 4 and 1 to 5 chelates with thorium, the former type could not be prepared by heating the latter as was done with the simple 8-quinolinol compounds.[1] Instead, separate reactions in the 1 to 4 and 1 to 5 stoichiometries under carefully controlled conditions were essential. For each compound, numerous experiments under a variety of conditions were carried out, the final set of conditions recommended being those which gave products of the highest purity with quantitative thorium recovery. In no instance did the difficulties of manipulation permit preparation of more than one gram of product in a single batch. All products were anlyzed for thorium by ignition of weighed samples to the dioxide and for carbon, hydrogen, nitrogen and halogen by the usual microanalytical techniques

Optimum conditions of *p*H, acetone concentration, and filtration varied with each chelate, but the following general procedure is applicable to all materials: Twenty ml. of thorium nitrate solution (equivalent to 0.1098 g. of thorium) is diluted to 200 ml., and 5 ml. of 12 *M* hydrochloric acid solution is added. To this solution is added the calculated quantity of 8-quinolinol reagent in acetone. The *p*H is raised to the optimum value (*e.g.*, 3.0 for $Th(C_9H_4Cl_2NO)_4$–$C_9H_4Cl_2NOH$, 9.0 for $Th(C_9H_4Cl_2NO)_4$) by slow addition first of 6 *M* aqueous ammonia and then of 1 *M* aqueous ammonia with vigorous mechanical stirring. The acetone concentration is reduced to 30–40% by dilution with water. Stirring is continued for 10–15 min., and the suspension is digested 10–15 min. on the steam-bath, evaporation of acetone being minimized by covering the container with a watch glass. The cooled suspension is filtered through a medium porosity sintered glass crucible and the product washed until chloride-free with 20% acetone in water and dried for 1–2 hr. (85–90° for 1 to 5 chelates, 100–120° for 1 to 4 chelates).

Anal. Calcd. for $Th(C_9H_4Cl_2NO)_4$: C, 39.90; H, 1.49; N, 5.17; Cl, 26.18; Th, 21.41. Found: C, 39.10; H, 1.81; N, 4.91; Cl, 28.05; Th, 21.54. Calcd. for $Th(C_9H_4Cl_2NO)_4 \cdot C_9H_4Cl_2NOH$: C, 41.64; H, 1.63; N, 5.40; Cl, 27.32; Th, 17.88. Found: C, 40.72; H, 1.81; N, 5.42; Cl, 28.06; Th, 18.35.

Calcd. for $Th(C_3H_4Br_2NO)_4$: C, 30.03; H, 1.12; N, 3.89; Br, 44.40; Th, 16.12. Found: C, 30.36; H, 1.72; N, 3.62; Br, 46.23; Th, 16.50. Calcd. for $Th(C_9H_4Br_2NO)_4 \cdot C_9H_4Br_2NOH$: C, 31.02; H, 1.22; N, 4.02; Br, 45.85; Th, 13.32. Found: C, 30.96; H, 1.19; N, 3.95; Br, 46.98; Th, 13.16.

Calcd. for $Th(C_9H_4ClINO)_4$: C, 29.82; H, 1.11; N, 3.86; Th, 16.00. Found: C, 27.43; H, 1.86; N, 3.25; Th, 16.10. Calcd. for $Th(C_9H_4ClINO)_4 \cdot C_9H_4ClINOH$: C, 30.79; H, 1.21; N, 3.99; Th, 13.21. Found: C, 28.53; H, 1.34; N, 3.53; Th, 13.10.

Absorption Spectra Measurements.—All solutions for these studies were prepared in the dark room under red light[1] from weighed samples of the chelates. These solutions were protected from light until measured in the spectrophotometer. Under these conditions, photochemical decompositions were not observed.

Results and Discussion

Because of reduced solubilities of the reagents over that of 8-quinolinol, optimum conditions for the preparation of the thorium chelates require the presence of large quantities of acetone. Analytical results indicate the formation of both 1 to 4 and 1 to 5 chelates. Although the latter do decompose thermally at temperatures above *ca.* 85–90°, quantitative conversion to the 1 to 4 chelates was never effected by heating. The dihalo compounds are thermally more stable than the unsubstituted 8-quinolinol chelates.[1]

Absorption Spectra Studies.—Spectrophotometric data for chloroform solutions of these chelates paralleled closely those previously obtained[1] for the simple 8-quinolinol chelates, except for measurable bathochromic shifts in absorption bands. Comparable shifts appear in the spectra of other 5,7-dihalo-8-quinolinol chelates.[6,7] In every instance, spectra for solutions of the 1 to 4 and the 1 to 5 compounds differed only in intensities,[1] increased absorptions with the 1 to 5 materials corresponding closely to those produced by adding the free 8-quinolinol type reagent to the 1 to 4 compound in a 1 to 1 mole ratio.[1] These behaviors parallel exactly those reported for the unsubstituted 8-quinolinol chelates of thorium[1] and suggest strongly that the extra mole of reagent in the solid 1 to 5 compound is in every instance held loosely and lost upon dissolution. The view that the material is held by lattice forces[1] is not inconsistent with the data.

Spectra of chloroform solutions of these chelates were comparable with those of hydrolytically decomposed 8-quinolinol chelates[1] but indicated such decompositions to be less pronounced. In no case was rigorous adherence to Beer's law noted. However, when chloroform was stored overnight over anhydrous calcium chloride, refluxed for two hours, and then doubly distilled, it yielded solutions for which light absorptions deviated much less from Beer's law. Data for the 1 to 4 5,7-dichloro-8-quinolinol chelate as a typical case are given in Fig. 1. The extreme water sensitivities of such solutions are apparent.

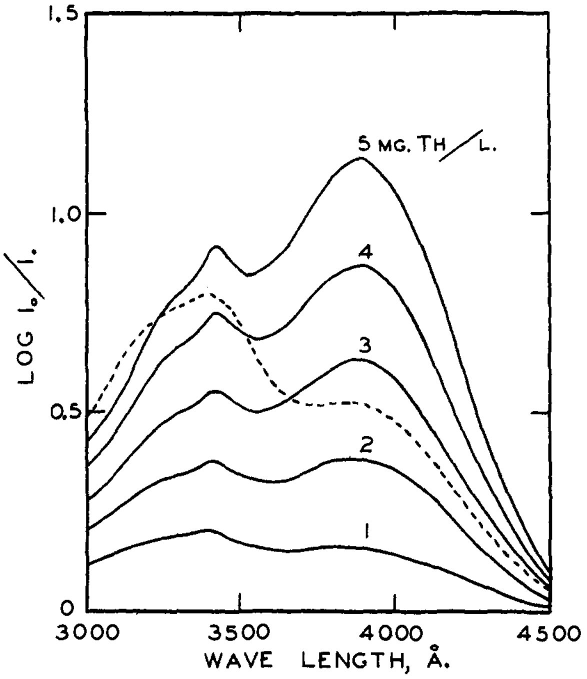

Fig. 1.—Absorption spectra of solutions of $Th(C_9H_4Cl_2NO)_4$ in rigorously dried chloroform: dotted curve, 5 mg. Th/l. plus 1 drop of water; cell length, 5.0 cm.; temperature, *ca.* 25°; concentrations as given with curves.

As was found with the 8-quinolinol chelates of thorium,[1] hydrolytic decompositions in ethanol solutions are much less striking. Solutions of the

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(6) F. L. Pundsack, Doctoral Dissertation, University of Illinois, 1952.

(7) T. Moeller and A. J. Cohen, *Anal. Chim. Acta*, **4**, 316 (1950).

5,7-dihalo-8-quinolinol chelates in absolute ethanol which had been dried over calcium oxide and doubly distilled gave only minor deviations from Beer's law. This is shown by the following data: $Th(C_9H_4Cl_2NO)_4$: 1–5 mg. Th/l., k_{av}[8] at 3420 Å. = 38.7, k_{av} at 3860 Å. = 58.1; $Th(C_9H_4Cl_2NO)_4 \cdot C_9H_4Cl_2NOH$: 1–5 mg. Th/l., k_{av} at 3420 Å. = 49.9, k_{av} at 3860 Å. = 66.1; $Th(C_9H_4Br_2NO)_4$: 2–5 mg. Th/l., k_{av} at 3420 Å. = 41.8, k_{av} at 3880 Å. = 62.0; $Th(C_9H_4Br_2NO)_4 \cdot C_9H_4Br_2NOH$: 1–5 mg. Th/l., k_{av} at 3420 Å. = 56.7, k_{av} at 3880 Å. = 64.6; $Th(C_9H_4ClINO)_4$: 1–5 mg. Th/l., k_{av} at 3460 Å. = 42.1, k_{av} at 3920 Å. = 47.0; $Th(C_9H_4ClINO)_4 \cdot C_9H_4ClINOH$; 1–5 mg. Th/l., k_{av} at 3460 Å. = 53.2, k_{av} at 3920 Å. = 54.2.

The enhanced resistance of ethanol solutions to water is indicated clearly by the typical data for the 1 to 4 dichloro chelate as given in Fig. 2. As much as 10% water by volume has less effect upon ethanol solutions than 0.1% water by volume has upon chloroform solutions. Even though the 5,7-dihalo-8-quinolinol chelates have reduced water sensitivities, they are still sufficiently strongly hydrolyzed to be of doubtful utility for spectrophotometric determinations of thorium.

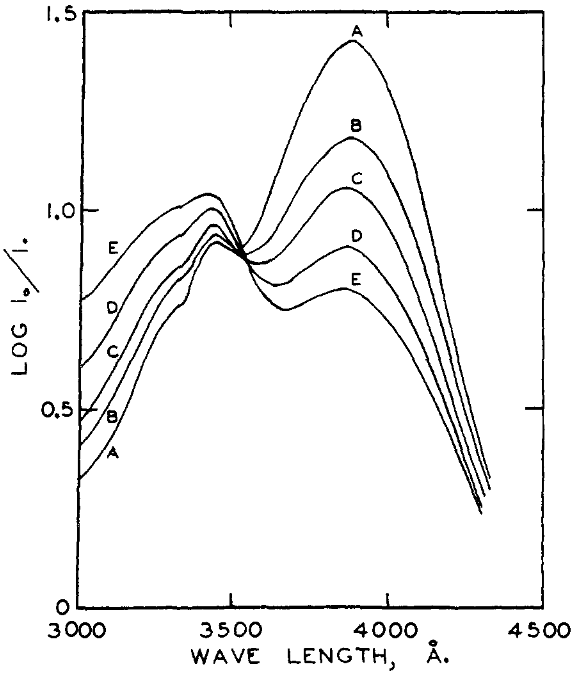

Fig. 2.—Effect of water upon absorption spectra of ethanol solutions of $Th(C_9H_4Cl_2NO)_4$: A, no water; B, 2% water by volume; C, 4% water by volume; D, 12% water by volume; E, 20% water by volume. 5 mg. Th/l. in each case; cell length, 5.0 cm.; temperature, *ca.* 25°.

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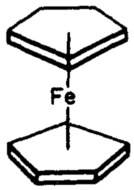
[8] Specific extinction, k, is given by the relationship $k = (\log I_0/I)/cl$, l being in cm. and c being expressed as g. Th/liter.

Bis-indenyl Derivatives of Iron and Cobalt

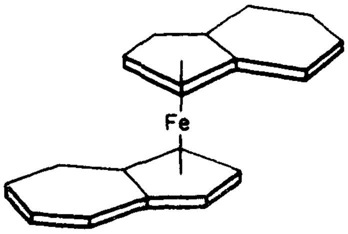
BY P. L. PAUSON AND G. WILKINSON

RECEIVED SEPTEMBER 2, 1953

The discovery of the reaction[1] of cyclopentadienylmagnesium bromide with ferric chloride to yield ferrocene (A) has been followed by the preparation of numerous analogous compounds in which the iron is replaced by other transition metals.[2] In all these cases the cyclopentadiene ring is the characteristic common feature. The present results show that analogous, but somewhat less stable compounds may be derived from indene ("benzocyclopentadiene").



A



B

Thus indenyllithium reacts smoothly with ferric chloride to yield bis-indenyliron(II) or "dibenzferrocene" (B). Figure 1A shows the characteristic infrared spectrum of the deep purple crystals thus obtained. The compound is diamagnetic.

The preparation of the cobalt compound followed the method previously used for the preparation of cobalticinium salts,[3] cobalt(III) acetylacetonate being added to a solution of indenylmagnesium bromide. After decomposing the reaction mixture with ice–hydrochloric acid, salts of the bis-indenylcobalt(III) ion readily can be obtained from the aqueous layer. Like the cobalticinium ion, the "dibenzocobalticinium ion" may be precipitated as the triiodide, tribromide, picrate, reineckate, silicotungstate, etc. The perchlorate is also sparingly soluble in water. Both the picrate and perchlorate have been obtained pure by crystallization from water. Both show remarkably high solubility in polar organic solvents. Figure 1 (B and C) shows the infrared spectra of the perchlorate and triiodide. The strong absorption of the former in the 9μ region is the known absorption of the anion[4]; however, other differences caused by the change of anion, particularly the displacements of the strong peaks at 11.6–11.8 and 13.1–13.3μ appear noteworthy.

On reduction at the dropping mercury electrode, the bis-indenylcobalt(III) perchlorate, in a 0.1 *N* sodium perchlorate supporting electrolyte, shows a well-defined polarographic reduction wave at −0.6 volt *vs.* the standard calomel electrode. The corresponding half-wave potential for cobalticinium perchlorate[5] is −1.16 volt. Thus the annulation of a benzene ring causes a very marked decrease in the reduction potential and conversely

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[1] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[2] G. Wilkinson, P. L. Pauson and F. A. Cotton, THIS JOURNAL **76**, 1970 (1954), where complete references to earlier work are given

[3] G. Wilkinson, *ibid.*, **74**, 6148 (1952).

[4] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

[5] J. A. Page and G. Wilkinson, THIS JOURNAL, **74**, 6149 (1952).