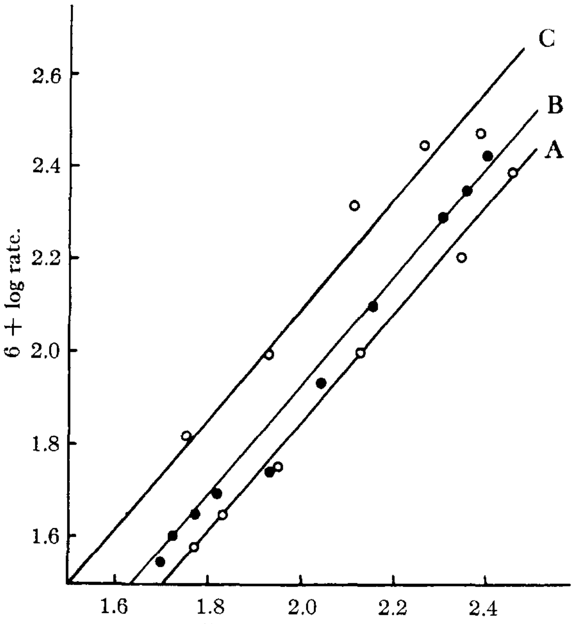


Fig. 1.—A, 4 *N* NaOH; B, 5 *N* NaOH; C, 7 *N* NaOH.

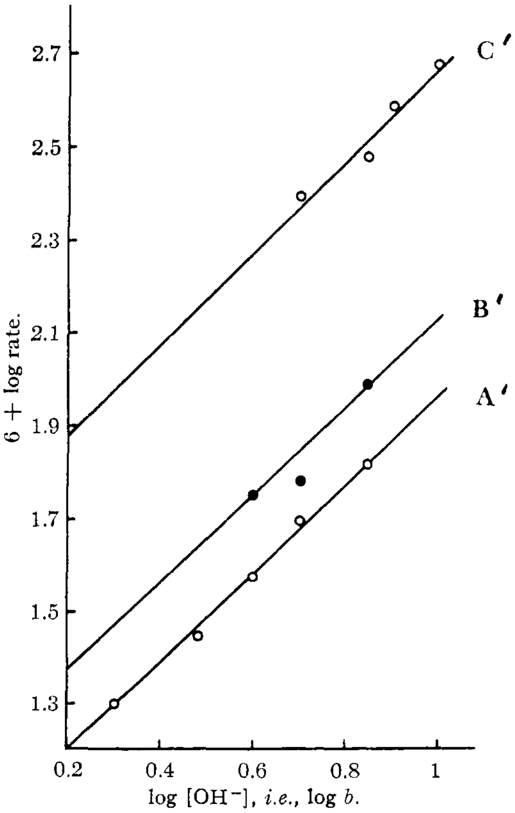


Fig. 2.—A′, 19 × 10^{-3} *M*; B′ = 11.3 × 10^{-3} *M*; C′ = 4.5 × 10^{-3} *M*.

Fig. 1 are obtained. The curves are linear with slopes amounting to 1.10, 1.15 and 1.10, respectively, indicating that the rate of decomposition depends on the permanganate concentration raised to a power of −1. Also by plotting log *r* against the logarithm of alkali concentrations *b* (for three different permanganate concentrations) curves A′, B′ and C′, of Fig. 2 are obtained. These curves also are linear, with the respective slopes of 0.95, 0.95 and 1 indicating a first-order reaction with respect to OH^- ions.

The role played by telluric acid is not very clear. Save for the fact that it dissolves the freshly precipitated manganese dioxide, nothing is known about its compounds with the higher oxidation states of manganese. In the reactions under hand, however, owing to the high alkalinity of the solutions, reduction of permanganate does not proceed below the manganate state (*cf.* ref. 4).

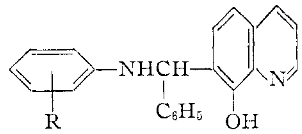
CHEMISTRY DEPARTMENT
FACULTY OF SCIENCE
CAIRO UNIVERSITY
GIZA, EGYPT

Chelate Compounds of 7-(α-Anilinobenzyl)-8-quinolinol

BY J. P. PHILLIPS AND A. L. DUCKWALL

RECEIVED JUNE 10, 1955

7-(α-Anilinobenzyl)-8-quinolinol (I, R = H) and derivatives in which the presence of the large 7-substituent might conceivably furnish an additional donor group for chelation as well as exert steric hindrance[1,2] form compounds with metal ions the compositions of which were determined in this investigation. The derivative (I, R = *o*-COOH) containing the chelating centers of both anthranilic acid and 8-quinolinol in one molecule is of particular interest because both the parent compounds are chelating agents of closely similar properties, and unusual behavior toward metals might be anticipated from the combination.[3] For comparative purposes two new compounds (I, R = *o*-$COOC_2H_5$, and R = *p*-COOH) were also prepared.



I

In general the chelate compounds of 7-(α-anilinobenzyl)-8-quinolinol were observed to have approximately the same colors (and sometimes fluorescence) as the corresponding 8-quinolinol compounds as well as the same ratio of metal to reagent (Table I), showing that the new reagent is apparently only bidentate in spite of the presence of the side chain nitrogen. However, some differences in the behavior of the new reagent as compared to 8-quinolinol were also noted. As expected from its higher molecular weight 7-(α-anilinobenzyl)-8-quinolinol gave precipitates with smaller amounts of metals in sensitivity tests with representative ions. Although the scandium compound of 8-quinolinol contains a molecule of added 8-quinolinol,[4,5] no such added reagent was observed with the new compound, possibly because of different experimental conditions (precipitation from a cold

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(1) H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 2910 (1954).

(2) R. Belcher, A. Sykes and J. C. Tatlow, *ibid.*, 376 (1955).

(3) J. F. Flagg, "Organic Reagents," Interscience Publishers, Inc., New York, N. Y., 1948, p. 76.

(4) T. Moeller and M. V. Ramaniah, THIS JOURNAL, **76**, 6030 (1954).

(5) L. Pokras and P. M. Bernays, *ibid.*, **73**, 7 (1951).

solution without excess reagent). The thorium compound analyzed for a greater metal content than corresponded to either the 1:4 or 1:5 mole ratio of metal to reagent expected by analogy with 8-quinolinol.[6] Inasmuch as the molecular weights of the expected thorium derivatives are above 1500, it is possible that failure to obtain them resulted from the insolubility of a high molecular weight intermediate basic compound.

7-[α-(*o*-Carboxyanilino)-benzyl]-8-quinolinol also gave chelate compounds of similar physical appearance to 8-quinolinol chelates. For trivalent ions the expected 1:3 ratio of metal to reagent was obtained, but for the divalent ions tested the metal content was high for the expected 1:2 mole ratio and, indeed, corresponded fairly well to a 1:1.5 ratio. It is possible that this ratio is fortuitous; at any rate the structures of these compounds have not been established. Partial formation of a salt of the carboxylic acid group along with the usual chelate bonding to the 8-quinolinol portion of the molecule might be responsible for this effect; however, it is significant that anthranilic acid is a good chelating agent for many divalent ions but has not been reported in the literature as giving chelate compounds with trivalent ions. The observed effect might then be attributed to a competition between the two chelating centers. This interpretation is further supported by the failure of the *p*-aminobenzoic acid (I, R = *p*-COOH) and ethyl anthranilate (I, R = *o*-$COOC_2H_5$) derivatives to form any "abnormal" chelate compositions.

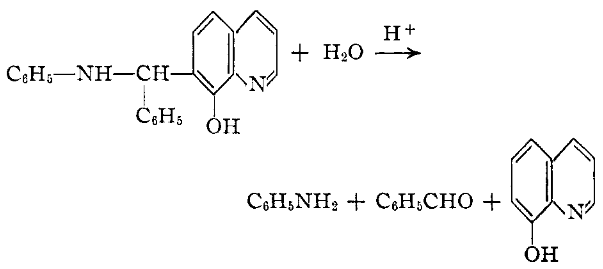
TABLE I

ANALYSIS OF METAL COMPOUNDS OF 7-(α-ANILINOBENZYL)-8-QUINOLINOL AND DERIVATIVES

Compd. formula	Metal	Metal, % Calcd.	Found (ignition)	Found (bromination)
A. 7-(α-Anilinobenzyl)-8-quinolinol				
$M(C_{22}H_{17}N_2O)_2$	Be	1.36		1.06, 1.04
	Mg	3.61	3.6, 3.5	
	Ca	5.8		5.8, 5.6
	Mn	7.8	8.3	7.9, 7.8
	Ni	8.3	8.2, 8.1[a]	8.4, 8.3, 8.2
	Cu	8.9	9.3, 9.1	
	Zn	9.1	9.2, 8.9	91., 9.0
	Pd	14.1	14.5[b]	
	Ba	17.5		17.5
$M(C_{22}H_{17}N_2O)_3$	Al	2.69	3.0, 2.6	
	Sc	4.4		4.3, 4.2
	Fe	5.4	5.2, 5.1	
	Ga	6.7		6.4
	Y	8.3		8.2, 8.2
	In	10.5		9.7
	La	12.5	11.6	
$UO_2(C_{22}H_{17}N_2O)_2 \cdot C_{22}H_{18}N_2O$	U	19.1	19.0	
$M(C_{22}H_{17}N_2O)_4$	Th	15.1	19.8, 19.8	
B. 7-[α-(*o*-Carbethoxyanilino)-benzyl]-8-quinolinol				
$M(C_{25}H_{21}N_2O_3)_2$	Mg	2.97		2.98, 2.96
	Ni	6.9		6.8, 6.8
	Cu	7.4	6.8	
	Zn	7.6		7.9
$M(C_{25}H_{21}N_2O_3)_3$	Al	2.22		2.18, 2.12
	Fe	4.5	4.1	
	Y	6.9		6.9, 6.9
C. 7[α-(*o*-Carboxyanilino)-benzyl]-8-quinolinol				
$M(C_{23}H_{17}N_2O_3)_{1.5}$	Mg	4.2	4.6	
	Mn	9.0		8.9, 8.9
	Cu	10.3	10.0[c]	
	Zn	10.5	11.2, 10.9	
	Pd	16.1	15.5[b]	
$M(C_{23}H_{17}N_2O_3)_3$	Al	2.38	2.00	2.16
	Fe	4.8	5.2	
	Y	7.4		7.1, 7.0
	In	9.4		8.6
D. 7-[α-(*p*-Carboxyanilinobenzyl]-8-quinolinol				
$M(C_{23}H_{17}N_2O_3)_2$	Cu	7.9	7.9	
	Zn	8.2	8.9	
$M(C_{23}H_{17}N_2O_3)_3$	Fe	4.8	5.3	

[a] Calculated as metal rather than oxide since complete reduction apparently occurred in crucible.[7] [b] Weighed as metal after reduction with formic acid. [c] Average of five results agreeing within 0.1%.

The metal compounds of 7-(α-anilinobenzyl)-8-quinolinol and derivatives were prepared at room temperature and filtered almost immediately because digestion at elevated temperature appeared to produce partial hydrolysis of the reagent, leading to high metal content in the precipitate. Since the reagent and its metal derivatives dissolved readily in 4 *N* hydrochloric acid, analysis of the compound structures by bromination was investigated using essentially the well-known procedure employed in analysis of 8-quinolinol. Results of brominating weighed samples of the reagent (Table II) showed that ten equivalents of bromine were consumed by each mole as a result of the hydrolysis



The aniline is then tribrominated and the 8-quinolinol dibrominated, both reactions being quantitative. This interpretation was supported by the isolation of 2,4,6-tribromoaniline from the reaction mixture, as well as by the odor of benzaldehyde. Although the bromination is accurate only to 1%, it is still very satisfactory because of the low metal content of the samples and the favorable equivalent weights (for divalent ions 5% of the atomic weights).

7-[α-(*o*-Carboxyanilino)-benzyl]-8-quinolinol also absorbed ten equivalents of bromine per mole, which is consistent with the known fact that anthranilic acid is quantitatively converted to 2,4,6-tribromoaniline by excess bromine.[8] 7-[α-(*o*-Carbethoxyanilino)-benzyl]-8-quinolinol absorbed only eight equivalents of bromine, a result indicating that the ester was not appreciably hydrolyzed to the acid

TABLE II

BROMINATION OF SUBSTITUTED 7-(α-ANILINOBENZYL)-8-QUINOLINOLS

Substituent in I	No. samples	Av. eq. bromine/mole	Av. dev.
R = H	10	10.00	0.08
o-COOH	7	10.01	.15
o-$COOC_2H_5$	4	8.07	.05

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(6) T. Moeller and M. V. Ramaniah, THIS JOURNAL, **75**, 3946 (1953).

(7) C. Duval, "Inorganic Thermogravimetric Analysis," Elsevier Publishing Co., New York, N. Y., 1953, p. 238.

(8) A. R. Day and W. T. Taggert, *Ind. Eng. Chem.*, **20**, 545 (1928).

in the time allowed for the reaction. The *p*-aminobenzoic acid derivative (I, R = *p*-COOH) could not be quantitatively brominated.

Some attempts to determine zinc quantitatively by bromination of its 7-(α-anilinobenzyl)-8-quinolinol derivative were made, but, although complete precipitation of zinc was obtained, the necessary use of excess reagent caused coprecipitation of reagent, leading to results that were high.

Experimental

Preparation of Reagents.—7-(α-Anilinobenzyl)-8-quinolinol and 7-[α-(*o*-carboxyanilino)-benzyl]-8-quinolinol were prepared by published methods.[9] Titration of 7-(α-anilinobenzyl)-8-quinolinol in glacial acetic acid with 0.1 *N* perchloric acid using a glass electrode gave a molecular weight of 325.4, assuming the compound is dibasic; calculated molecular weight is 326.4. Since similar titration of the anthranilic acid derivative did not give a satisfactory end-point, its molecular weight was obtained by the spectrophotometric picrate[10] method, giving for the molecular weight of the picrate 601; calcd., 599.

7-[α-(*o*-Carbethoxyanilino)-benzyl]-8-quinolinol was prepared by mixing 16.5 g. (0.1 mole) of ethyl anthranilate, 10.6 g. (0.1 mole) of benzaldehyde and 14.5 g. (0.1 mole) of 8-quinolinol in about 75 ml. of ethanol. After the stoppered flask had been standing for two days a white precipitate began to form which was filtered off after ten days and recrystallized from ethanol; yield 22 g. (55%); m.p. 135°.

Anal. Calcd. for $C_{25}H_{22}N_2O_3$: N, 7.03. Found: N, 7.08.

7-[α-(*p*-Carboxyanilino)-benzyl]-8-quinolinol was similarly obtained after 35 days from a mixture of 13.7 g. (0.1 mole) of *p*-aminobenzoic acid, 10.6 g. of benzaldehyde and 14.5 g. of 8-quinolinol in 300 ml. of ethanol. A cream-colored product, recrystallized from ethanol, was obtained; yield 16 g. (43%); m.p. 122°.

Anal. Calcd. for $C_{23}H_{18}N_2O_3$: N, 7.56. Found: N, 7.63.

Preparation of the Metal Chelate Compounds.—Approximately 0.01 molar solutions of the following ions in dilute acid were prepared from the pure metals or solid salts: Be^{+2}, Mg^{+2}, Ca^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2}, Pd^{+2}, Ba^{+2}, Pb^{+2}, UO_2^{+2}, Al^{+3}, Sc^{+3}, Fe^{+3}, Ga^{+3}, Y^{+3}, In^{+3}, La^{+3}, Ce^{+3}, Nd^{+3}, Sm^{+3}, Bi^{+3} and Th^{+4}.

Approximately 0.2-g. samples of each metal chelate compound were prepared from these solutions by adding the calculated amount of 7-(α-anilinobenzyl)-8-quinolinol (or derivative) in ethanol to a diluted solution of the metal ion, followed by addition of ammonium acetate, sodium acetate or ammonia as necessary to produce complete precipitation. The *p*H conditions used for 8-quinolinol precipitations generally sufficed, except that some of the 7-[α-(*o*-carboxyanilino)-benzyl]-8-quinolinol salts tended to redissolve in excess ammonia. After filtration the precipitates were washed thoroughly with water and generally given a final washing with a small portion of ethanol. Cerous and ferrous chelate compounds could not be satisfactorily prepared because the reagents oxidized these ions in nearly neutral solutions; compounds of 7-(α-anilinobenzyl)-8-quinolinol with cobalt, bismuth, lead, neodymium and samarium were prepared but not analyzed. Use of even a slight excess of reagent in these preparations was unsatisfactory because of its extreme insolubility in water.

Analyses.—For analysis of the metal compounds by the ignition method the entire 0.2-g. sample after drying at room temperature was ashed over a low flame and the oxide residue weighed after ignition under the usual conditions for the particular oxide. For the bromometric analyses 50-mg. samples were dissolved in 4 *N* hydrochloric acid by gentle heating for about five minutes. The solution was then cooled and diluted to about 100 ml. and an excess of 1–10 ml. of standard 0.1 *N* bromate–bromide solution added from a buret. The stoppered flask was allowed to stand for five minutes and then 0.5 g. of potassium iodide was added and the liberated iodine titrated after an additional five minutes with 0.05 *N* sodium thiosulfate to a starch–iodide end-point. A white precipitate of 2,4,6-tribromoaniline generally formed during the bromination and in one instance (titration of pure 7-(α-anilinobenzyl)-8-quinolinol) was filtered off, dried, and the m.p. determined to be 118°; reported m.p. of 2,4,6-tribromoaniline is 119°.

When analysis by both the ignition and bromination methods was desired, separately prepared samples of the metal compounds were used. In calculating the analytical results the possible presence of water of crystallization in some of the samples was not considered, because one or two molecules of water would have an almost negligible effect on the metal content owing to the large molecular weights of the metal compounds.

Sensitivity Tests.—These were performed by the method of Irving, Butler and Ring[11] using Al^{+3}, Fe^{+3}, Cu^{+2} and Ni^{+2} as representative ions. The sensitivities with 7-(α-anilinobenzyl)-8-quinolinol, expressed in micrograms per ml. were: Al^{+3}, 0.7; Fe^{+3}, 0.5; Cu^{+2}, 0.6 and Ni^{+2}, 0.3; with 7-[α-(*o*-carboxyanilino)-benzyl]-8-quinolinol, Al^{+3}, 1.5; Fe^{+3}, 0.5; Cu^{+2}, 0.1 and Ni^{+2}, 0.2.

Acknowledgments.—This work was supported by a grant from the National Science Foundation. Our thanks are also due to Misses Elizabeth Bryant and Mary Twickler for some of the preliminary work.

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(9) (a) F. Pirrone, *Gazz. chim. ital.*, **71**, 320 (1941); (b) J. Phillips, R. Keown and Q. Fernando, *J. Org. Chem.*, **19**, 907 (1954).

(10) K. G. Cunningham, W. Dawson and F. S. Spring, *J. Chem. Soc.*, 2305 (1951).

(11) H. Irving, E. J. Butler and M. F. Ring, *ibid.*, 1489 (1949).

CHEMISTRY DEPARTMENT
UNIVERSITY OF LOUISVILLE
LOUISVILLE, KENTUCKY

Studies on the Chemistry of Halogens and of Polyhalides. VI. Electrical Conductance of Polyhalogen Complexes in Ethylene Dichloride

BY ALEXANDER I. POPOV AND NORMAN E. SKELLY[1]

RECEIVED JUNE 27, 1955

Introduction.—Electrical conductance of several polyhalogen complexes has been recently determined in acetonitrile solutions.[2] The results obtained indicated that these complexes are strong electrolytes at least in solutions which are $\leqslant 10^{-1} M$. The work is now extended to ethylene dichloride solutions in order to see how the change in the dielectric constant of the solvent affects the conductance of these complexes. Ethylene dichloride was chosen because of its relatively low dielectric constant (10.23 *vs.* 36.5 for acetonitrile at 25°) and its ability to dissolve sufficient amounts of polyhalogen complexes for the conductance studies.

Experimental Part

Apparatus and Procedure.—The apparatus and the experimental procedure used in this investigation to obtain conductance measurements were discussed in an earlier paper.[2]

Polyhalogen Complexes.—Polyhalogen complexes studied in this work were tetramethylammonium iodobromochloride, tetrapropylammonium iododibromide, tetrabutylammonium iododichloride and the tetrabutylammonium tribromide. With the exception of the first compound it was found impossible to use the corresponding tetramethylammonium complexes because of their limited solubility in ethylene dichloride.

The first three compounds were prepared by the methods of Chattaway and Hoyle.[3] The tetrabutylammonium tribromide was supplied by Mr. L. Harris of this Laboratory. The purity of the compounds was checked by iodometric titration and found to be of the order of 98–99%. The

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(1) Du Pont pre-doctoral fellow 1953–1954.

(2) A. I. Popov and N. E. Skelly, THIS JOURNAL, **76**, 5309 (1954).

(3) F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).