

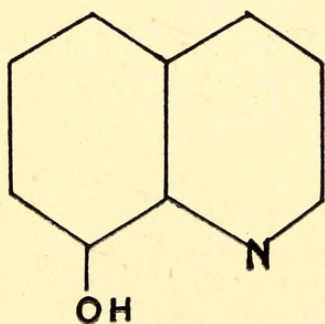
1-HYDROXYACRIDINE AS A CHELATE  
COMPOUND.By DOUGLAS HAIG FREEMAN, B.Sc.,  
and FRANCIS LIONS, B.Sc., Ph.D.

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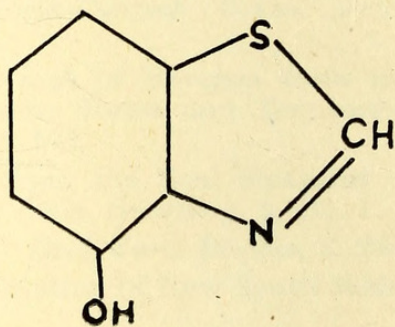
(Manuscript received, November 20, 1940. Read, December 4, 1940.)

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Bidentate chelate compounds which coordinate through one primary valency and one secondary valency very frequently form non-ionized metallic complexes—the so-called “internal complex salts”—many of which are distinguished by their insolubility in hydroxylic solvents. Such chelate compounds can, consequently, often be utilised in analytical chemistry for quantitative precipitation and estimation of certain metallic ions. Perhaps no such substance has proved of greater importance in recent years than 8-hydroxyquinoline (I)—“Oxine”.



I



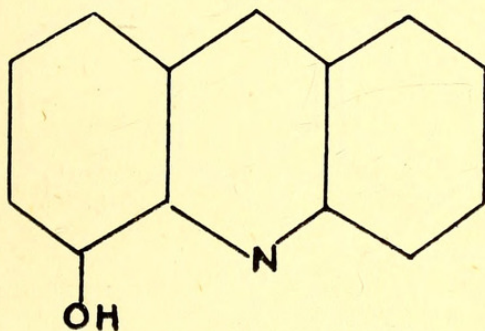
II

Numerous researches have thoroughly established its value in analytical chemistry (cf. e.g. Berg, *Z. Anal. Chem.*, 1927, 70, 341; 71, 23, 171, 321, 361; 72, 177; 1929, 76, 191; Hahn and Vieweg, *ibid.*, 1927, 70, 122; Hahn and Hartleb, *ibid.*, 71, 225; Kolthoff and Sandell, *J.A.C.S.*, 1928, 50, 1900; Niessner, *Z. Anal. Chem.*, 1929, 76, 135; Berg and Teitelbaum, *ibid.*, 1930, 81, 1; Geilmann and Weibke, *Z. Anorg. Chem.*, 1931, 199, 120, 347; Halberstadt, *Z. Anal. Chem.*, 1933, 92, 86; Fleck and Ward, *Analyst*, 1934, 59, 325).



The great usefulness of 8-hydroxyquinoline suggests that the juxtaposition of the phenolic hydroxyl group and the basic tertiary nitrogen atom of the attached fused heterocyclic ring, makes available a specially valuable chelate grouping and suggests the trial of similarly constituted substances. This idea has already been exploited by Erlenmeyer and Ueberwasser (*Helv. Chim. Acta*, 1938, 21, 1695; cf. also *Helv. Chim. Acta*, 1938, 21, 709), who prepared several metallic derivatives of 4-hydroxybenzthiazole (II), and showed that this substance was quite suitable for the quantitative estimation of zinc, copper and nickel.

The present paper records the results of some preliminary experiments with 1-hydroxyacridine (III) ("1-Acrinol"), which may be regarded as a "Benzoxine", and might well be expected to give co-ordination complexes similar



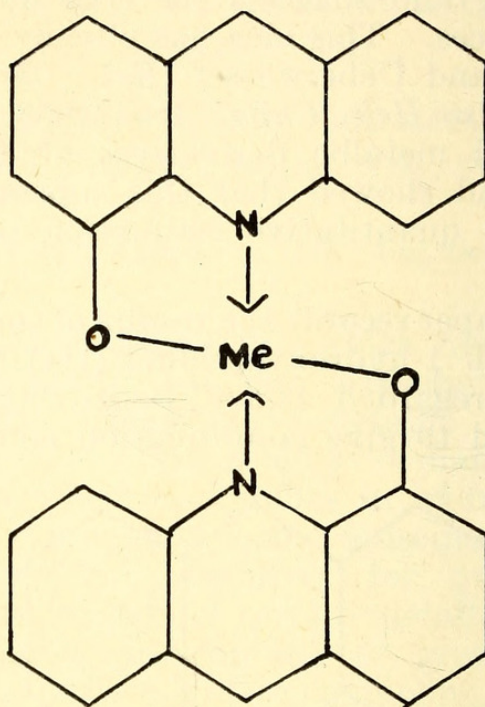
III

in type to those yielded by 8-hydroxyquinoline. An exhaustive study of 1-acridol (II) as a reagent in qualitative and quantitative analysis has not been carried out, but sufficient results have been accumulated to show that it does behave similarly to "Oxine" (II), forming numerous water-insoluble metallic complex derivatives, whilst, at the same time, differing from II in its behaviour to certain metallic ions, notably that of aluminium. It seems, therefore, that 1-acridol may prove to be a supplementary reagent in analysis of some value, and since one of the authors is unable to continue the work it is deemed advisable to place the results so far obtained on record.

Treatment of dilute aqueous solutions, containing also sodium acetate and acetic acid, of salts of the metals listed below with 2% alcoholic 1-acridol solution led to precipitation of insoluble metallic complexes: copper, zinc, lead, nickel, ferrous iron, ferric iron, chromium, cobalt, cadmium,



manganese, mercury and thallium. Careful analysis showed that the complexes derived from copper, lead, zinc, nickel and ferrous salts are of the type IV, the metal being

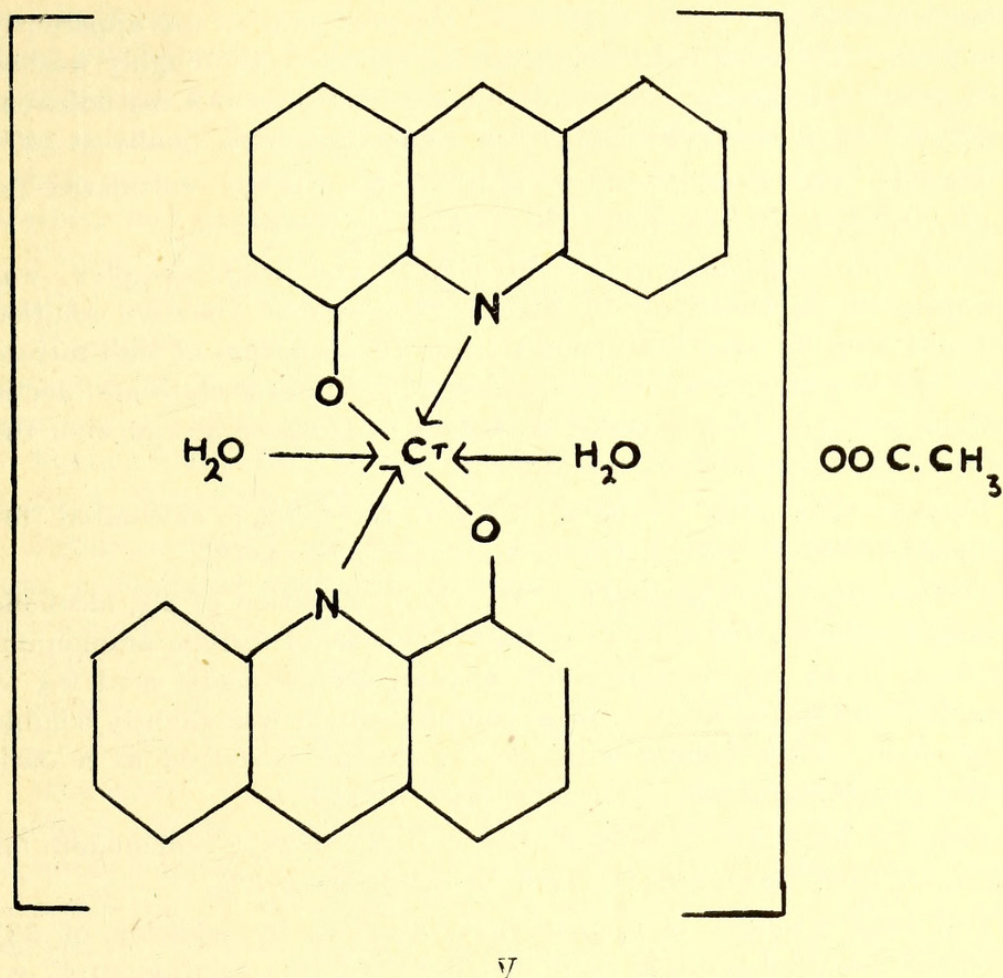


IV

quadricovalent. The complex derived from ferric salts was apparently identical with that derived from ferrous salts, reduction by some of the 1-acridol of the ferric ion to the ferrous state apparently preceding co-ordination. Oxidation of 1-acridol also appeared to occur with silver salts, the dark brown insoluble silver complex precipitated from weakly acid acetate solution being found to contain free silver, and to be of indefinite composition.

The analytical figures obtained for the complexes precipitated from cobaltous, cadmium and manganous salt solutions, indicated that these also were probably of type IV, but in each instance the values found for carbon and nitrogen were considerably lower than theoretical. It is also possible that the salts of type IV were contaminated with basic salts, but insufficient results are available for any definite conclusion concerning the low analytical figures. The chromium complex appeared to be of the type V, similar to the chromium complexes described by Drew and Fairbairn (*J.C.S.*, 1939, 823-35).





## EXPERIMENTAL.

*1-Acridol.* Two methods for the preparation of 1-acridol appear to have been recently described—by Matsumura (*J.A.C.S.*, 1927, 49, 816) and by Jensen (*J.A.C.S.*, 1928, 50, 1144). Eventually 1-acridol was prepared by a modification of Matsumura's method. The starting material, o-anisidine, was converted to 1-methoxyacridine, and by heating this with large quantities of hydriodic acid 1-acridol was obtained in 60% yield. After repeated recrystallisation from 75% aqueous alcohol it formed yellow crystals melting at 116°.

In the preparation of the metallic complexes of 1-acridol a procedure similar to that recorded for the precipitation of metallic complexes with 8-hydroxyquinoline was employed. The method is indicated in the description of the precipitation of the copper complex.

*Copper Bis 1-Acridylate (IV. Me=Cu.)* Sodium acetate (15 g.) and glacial acetic acid (15 ml.) were added to a solution of crystalline copper sulphate (1.18 g.) in water (300 ml.) at approximately 60°. A 2% alcoholic 1-acridol solution was then stirred in, drop by drop, until it was present in slight excess (up to 10% excess), and the temper-



ature was gradually raised to 90° when the precipitation was apparently complete. The dark red precipitate was collected, thoroughly washed with hot water, then extracted with hot alcohol (to remove any adherent 1-acridol), again washed with hot water and then dried, finally at 140°.

Found: Cu=13.7, C=68.9, H=3.7, N=6.1%; calculated for  $C_{26}H_{16}O_2N_2Cu$ , Cu=14.1, C=69.1, H=3.5, N=6.2%.

*Lead Bis-1-Acridylate (IV. Me=Pb.)* The lead complex was precipitated quantitatively by adding 2% alcoholic 1-acridol solution (80 ml.) drop by drop with good stirring to a solution of lead nitrate (0.93 g.) in water (200 ml.) containing 5% sodium acetate and acetic acid as before. After washing as before with water and alcohol the rust-red granular product was dried at 110°.

Found: Pb=34.9, C=53.2, H=2.7, N=4.7%; calculated for  $C_{26}H_{16}O_2N_2Pb$ , Pb=34.8, C=52.4, H=2.7, N=4.7%.

*Ferrous Bis-1-Acridylate (IV. Me=Fe.)* Addition of 2% alcoholic 1-acridol solution (50 ml.) to a dilute solution of ferrous ammonium sulphate (1.41 g.) containing 5% sodium acetate-acetic acid led to complete precipitation of a black complex which was slightly soluble in alcohol. After boiling with alcohol it was recovered as a dark brown product and was eventually dried at 110°.

Found: Fe=11.7, C=68.9, H=3.7, N=6.2%; calculated for  $C_{26}H_{16}O_2N_2Fe$ , Fe=12.6, C=70.3, H=3.6, N=6.3%.

The same product was apparently obtained by addition of 2% alcoholic 1-acridol solution to dilute ferric chloride solution (0.47 g.,  $FeCl_3 \cdot 6H_2O$  in water (200 ml.) containing 5% sodium acetate-acetic acid) or to a similar ferric alum solution. In each instance a black precipitate slightly soluble in alcohol was thrown down.

Found: Fe=11.8, C=68.2, H=3.6, N=6.1%; calculated for  $C_{26}H_{16}O_2N_2Fe$ , Fe=12.6, C=70.3, H=3.6, N=6.3%.

*Nickel Bis-1-Acridylate (IV. Me=Ni.)* The nickel complex came down, apparently quantitatively, as a deep red precipitate. After washing and drying at 110° it was analysed.

Found: Ni=11.4, C=67.7, H=3.8, N=6.0%; calculated for  $C_{26}H_{16}O_2N_2Ni \cdot H_2O$ , Ni=12.6, C=67.1, H=3.9, N=6.0%.

It appears, therefore, to contain one molecule of water of crystallisation.

*Zinc Bis-1-Acridylate (IV. Me=Zn.)* This zinc complex was precipitated by the standard method as an orange powder, and did not appear to come down completely. After washing and drying at 110° it was analysed.

Found: Zn=15.6, C=64.3, H=3.7, N=5.6%; calculated for  $C_{26}H_{16}O_2N_2Zn \cdot 2H_2O$ , Zn=13.3, C=63.8, H=4.1, N=5.7%.

It would appear, therefore, that this zinc complex contains two molecules of water of crystallisation, but owing to the incomplete



precipitation it is possible that some proportion of a basic salt has been precipitated and is contaminating the main product.

*Cobaltous Bis-1-Acridylate (IV. Me=Co.)* An orange precipitate was thrown down apparently quantitatively from buffered dilute cobalt acetate solution with alcoholic 2% 1-acridol solution. After washing and drying at 110° it was analysed.

Found: Co=13.2, C=65.3, H=3.6, N=5.7%; calculated for  $C_{26}H_{16}O_2N_2Co$ , Co=13.2, C=69.8, H=3.6, N=6.3%.

*Manganous Bis-1-Acridylate (IV. Me=Mn.)* The manganous complex of 1-acridol was a mustard coloured compound. After washing and drying at 110° it was analysed.

Found: Mn=13.2, C=64.2, H=3.6, N=5.8%; calculated for  $C_{26}H_{16}O_2N_2Mn$ , Mn=12.4, C=70.4, H=3.6, N=6.3%.

*Cadmium Bis-1-Acridylate (IV. Me=Cd.)* The cadmium complex was precipitated apparently quantitatively from buffered cadmium acetate solution as a bright orange powder. After washing and drying at 110° it was analysed.

Found: Cd=21.7, C=54.4, H=3.0, N=4.6%; calculated for  $C_{26}H_{16}O_2N_2Cd$ , Cd=22.3, C=62.4, H=3.2, N=5.6%.

*Chromium Complex with 1-Acridol (V).* 2% alcoholic 1-acridol solution (50 ml.) was gradually added to a well stirred solution of chromic sulphate (0.86 g.), sodium acetate (10 g.) and glacial acetic acid (10 ml.) in water (200 ml.). A dark red complex salt was precipitated. It was collected, washed thoroughly with water, and then recrystallised from alcohol and finally dried at 110°.

Found: Cr=11.8, C=61.9, H=3.9, N=5.2%; calculated for  $C_{28}H_{23}O_6N_2Cr$ , Cr=9.9, C=62.8, H=4.3, N=5.2%.

*Complexes of 1-Acridol with other Metallic Ions.* Silver acetate solution readily formed a dark brown precipitate with alcoholic 2% 1-acridol solution, but the collected washed and dried precipitate contained over 50% of silver, indicating reduction of some of the silver salt and precipitation of free silver.

In order to ascertain whether complex formation resulted with other metal ions, a few drops of 2% alcoholic 1-acridol solution were added to dilute solutions of several metallic salts, and it was observed that whilst precipitates formed in them under alkaline or neutral conditions these precipitates were sometimes soluble in a solution containing also sodium acetate and acetic acid.

#### (a) Precipitates Insoluble in Dilute Acetic Acid-Sodium Acetate Solution.

1. Hg+ from mercurous nitrate—deep red gelatinous precipitate.
2. Hg++ from mercuric chloride—light orange precipitate.
3. Tl++ from potassium thallium bromide—brown precipitate.



(b) **Precipitates from Neutral Solution—Soluble in Dilute Acetic Acid-Sodium Acetate Solution.**

1.  $\text{Ca}++$  from calcium chloride—yellow precipitate.
2.  $\text{UO}_2++$  from uranylacetate—deep red precipitate.

(c) **Precipitates from Alkaline Solution—Soluble in Dilute Acetic Acid-Sodium Acetate Solution.**

1.  $\text{Ba}++$  from baryta—orange precipitate.
2.  $\text{Ca}++$  from lime water—yellow precipitate.
3.  $\text{Mg}++$  from magnesium chloride solution containing ammonium chloride and ammonium hydroxide—yellow precipitate.

Some experiments designed to test roughly the sensitivity of 1-acridol as a reagent for the precipitation of certain metallic ions showed that lead in concentrations as low as  $10^{-4}$  grams per ml. and copper in concentrations as low as  $10^{-6}$  grams per ml. gave definite precipitates.

Finally, it should be noted that precipitates could not be obtained from 1-acridol with salts of aluminium, stannous tin, or bismuth, which is quite remarkable because each of them combines freely with 8-hydroxyquinoline.

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Freeman, Douglas Haig and Lions, Francis. 1941. "1-hydroxyacridine as a chelate compound." *Journal and proceedings of the Royal Society of New South Wales* 74(4), 520–526. <https://doi.org/10.5962/p.360318>.

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