[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Formazyl Complexes of the Quinoline Series

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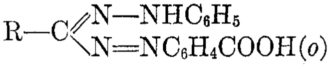
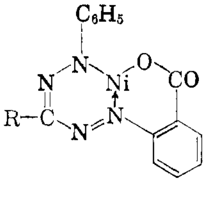
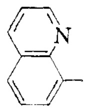
Three formazyl compounds of the general formula $C_6H_5NH—N=CR—N=NC_6H_4COOH$ are described where R represents various quinoline radicals and the carboxy group is in the *ortho* position relative to the formazan chain. These compounds form well defined complexes with nickel and uranyl ions. Three formazyl compounds of the type $C_6H_5NH—N=CR—N=NC_6H_5$ are also described. These do not form nickel and uranyl derivatives but those where R = 6-methyl- and 7-methyl-2-quinolyl readily form addition compounds with $CoCl_2$.

Formazyl compounds with a carboxy group in the *ortho* position relative to the formazan chain have pronounced complex-forming ability. A series of such complexes derived from the basic substance  $R—C\begin{matrix}\diagup N—NHC_6H_5 \\ \diagdown N=NC_6H_4COOH(o)\end{matrix}$ where R represents a heterocyclic radical, have been described in recent times.[2] The formation of complexes results through the substitution of hydrogen from the imino and carboxy groups by metal ions in alcohol solution. In most of the complexes which have been investigated the metal exhibits a smaller coordination number than the usual one. For example, in all nickel complexes it appears that only three of the coordinating positions of nickel are occupied[2e, f, g] while in the uranium complexes the uranium exhibits in some cases the usual coordination number of 6[2b, d] and in others, by contrast, the apparent coordination number 5.[2a, c] In all of the formazyl complexes so far investigated which are derived from the above parent substance, only the substituent R on the carbon atom of the formazan chain was different. Consequently, one is led to think that the indefiniteness of the coordination number of the uranium complexes must be dependent upon the nature of the R group. For the further clarification of this behavior, three new formazyl compounds have been prepared with R = 8-quinolyl(I), 6-methyl-2-quinolyl(II), and 7-methyl-2-quinolyl(III). These form with nickel sulfate in alcoholic solution highly colored crystalline complexes whose analyses are consistent with the formulas IA, IIA, and IIIA.

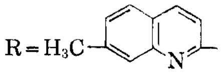
The formazyl compounds were prepared by coupling diazotized anthranilic acid with the corresponding aldehyde-phenylhydrazone in strongly alkaline solution: 8-quinolinecarboxaldehyde,[3] 6-methyl-2-quinolinecarboxaldehyde,[4] and 7-methyl-2-quinolinecarboxaldehyde.[5] As expected, in all of the nickel complexes, the nickel is linked with only three ligands.



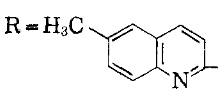
IA: R =



IIIA:

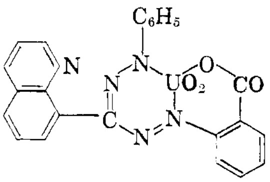


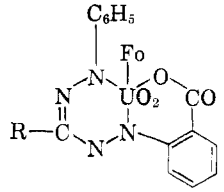
IIA:



The same formazyl compounds form with uranyl acetate in alcoholic solution, the uranium complexes of the constitutional formulas IB, IIB, and IIIB.

IB,





IIB, R = 6-methyl-2-quinolyl
IIIB, R = 7-methyl-2-quinolyl

The symbol Fo in formulas IIB and IIIB signifies a molecule of the corresponding formazyl compound attached to the uranium atoms. While the precipitation of the uranium complexes IIB and IIIB results spontaneously from bringing together the alcoholic solutions of the component, the formation of IB requires some time.

As the above structural formulas show, the uranium in IB manifests the coordination number 5 and

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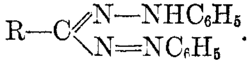
[2] (a) M. Seyhan, *Chem. Ber.*, **87**, 396 (1954); (b) *Chem. Ber.*, **87**, 1124 (1954); (c) *Chem. Ber.*, **88**, 212 (1955); (d) *Chem. Ber.*, **88**, 646 (1955); (e) *Chem. Ber.*, **88**, 1454 (1955); (f) *Monatsh.*, **86**, 545 (1955); (g) *Monatsh.*, **87**, 234 (1956); (h) M. Seyhan and W. C. Fernelius, *Chem. Ber.*, **89**, 2482 (1956).

[3] V. M. Radionov and M. A. Berkengeim, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 330–6 (1944); [*Chem. Abstr.*, **39**, 4077 (1945)]; F. Gialdi and R. Ponci, *Farm. sci. e tec.* (*Pavia*), **6**, 327–31 (1951); [*Chem. Abstr.*, **45**, 9117 (1951)].

[4] C. A. Bühler and S. P. Edwards, *J. Am. Chem. Soc.*, **74**, 978 (1952).

[5] M. Seyhan and W. C. Fernelius, *Chem. Ber.*, **89**, 2212 (1956).

in IIB and IIIB the coordination number 6. Whether the position of the ring nitrogen is the answer to the lack of the agreement of the coordination number or whether the presence of the methyl group exerts an influence cannot be said with certainty. For a definite assertion concerning such relationships, other methods of investigation must be employed.

An investigation was also undertaken with formazyl compounds not substituted in the *o*- position, *i.e.*, of the following type  $\mathrm{R{-}C}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{N{-}NHC_6H_5}}{\diagdown \mathrm{N{=}NC_6H_5}}$. The formazyl compounds which resulted from the coupling of diazotized aniline with the corresponding aldehyde-phenylhydrazone in strongly alkaline solution show no especial tendency for the formation of uranium or nickel complexes. The formazyls where R = 6- and 7-methyl-2-quinolyl (V and VI, respectively) yield in alcoholic solution with $CoCl_2 \cdot 6H_2O$ dark green crystals of the composition: formazyl·$CoCl_2$ while the formazyl where R = 8-quinolyl(IV) forms no such complex with cobalt(II) chloride.

EXPERIMENTAL[7]

8-Quinolinecarboxaldehyde.[3] A mixture of 10 g. 8-methylquinoline (b.p.$_{27}$ 132°) and 8.5 g. freshly prepared and unsublimed selenium dioxide was cautiously heated to 180–190° for 2 hr. using an air condenser. After cooling, the mixture, which in the meantime had solidified to a yellowish mass, was dissolved in 40 ml. 1:1 hydrochloric acid, filtered from the separated metallic selenium and decolorized with animal charcoal. Upon making the filtrate alkaline, the aldehyde precipitates as yellowish crystals: m.p. 92–93°. Yield 5.1 g.

8-Quinolinecarboxaldehydephenylhydrazone.[6] Yellow crystals from alcohol, m.p. 176°.

6-Methyl-2-quinolinecarboxaldehyde.[4] To a warm solution of 11 g. freshly prepared and unsublimed selenium dioxide in 100 ml. dioxane containing 4% water was added a solution of 11 g. 2,6-dimethylquinoline in 30 ml. dioxane. After 2 hr. heating under reflux, colorless crystals (m.p. 108–109°) were obtained by steam distillation. Yield 4.4 g.

6-Methyl-2-quinolinecarboxaldehydephenylhydrazone. Yellow crystals from alcohol, m.p. 198–199°.

Anal. Calcd. for $C_{17}H_{15}N_3$: N, 16.08. Found: N, 16.08.

6-Methyl-2-quinolinecarboxaldehyde-4-nitrophenylhydrazone. Dark yellow crystals from alcohol, m.p. 269–270°.

Anal. Calcd. for $C_{17}H_{14}N_4O_2$: N, 18.29. Found: N, 18.29.

6-Methyl-2-quinolinecarboxaldehyde-2,4-dinitrophenylhydrazone. Dark yellow crystals from alcohol, m.p. 252–253°.

Anal. Calcd. for $C_{17}H_{13}N_5O_4$: N, 19.94. Found: N, 20.12.

7-Methyl-2-quinolinecarboxaldehyde.[5] The oxidation of 1.7 g. 2,7-dimethylquinoline with 3.0 g. selenium dioxide gave colorless crystals, m.p. 69–70°. Yield 0.6 g.

7-Methyl-2-quinolinecarboxaldehyde-2-phenylhydrazone.[5] Yellow crystals from alcohol, m.p. 202–203°.

C-Substituted N-phenyl-N'-[2-carboxyphenyl]formazans (I–III). Five hundred fifty milligrams of anthranilic acid was dissolved in 2 ml. concentrated hydrochloric acid and diazotized with a concentrated solution of 340 mg. $NaNO_2$ at −5°. The diazonium solution was added to one of 770 mg. 8-quinolinecarboxaldehyde phenylhydrazone and 800 mg. sodium hydroxide in 120 ml. methanol at 0°. The mixture became red immediately. After 4 hr. it was filtered from some separated 8-quinolinecarboxaldehyde phenylhydrazone and acidified with glacial acetic acid. Upon the addition of water the red formazyl compound precipitated. It was recrystallized from alcohol.

The analogous formazans were prepared in the same manner using the corresponding aldehyde phenylhydrazones (Table I).

C-Substituted N,N'-diphenylformazans (IV–VI). One hundred milligrams of diazotized aniline was coupled with a strongly alkaline methanol solution of 200 mg. 8-quinolinecarboxaldehyde phenylhydrazone. After 3 hr. the mixture was filtered and the clear red solution acidified with acetic acid. Upon the addition of water, IV precipitated as red crystals. Upon the addition of 20% perchloric acid to the acetic acid solution of IV, the perchlorate precipitates as dark red crystals.

The analogous formazans were prepared in the same manner using the corresponding aldehyde phenylhydrazones (Table II).

TABLE I

C-SUBSTITUTED *N*-PHENYL-*N'*-[2-CARBOXYPHENYL]FORMAZANS

Compound	Anthranilic Acid, Mg.	Aldehyde, Mg.	Yield, Mg.	M.P., °C.	Calcd. Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
I	550	770	660	208–209 (d)	$C_{23}H_{17}N_5O_2$			17.71			17.61
II	225	340	225	186 (d)	$C_{24}H_{19}N_5O_2$	70.39	4.68	17.10	70.57	4.88	17.08
III	225	340	380	200 (d)	$C_{24}H_{19}N_5O_2$	70.39	4.68	17.10	70.01	4.86	17.31

TABLE II

C-SUBSTITUTED *N,N'*-DIPHENYLFORMAZANS

Compound	Aniline, Mg.	Aldehyde, Mg.	Yield, Mg.	$HClO_4$ Salt, M.P., °C.	Formula	Calcd. C	Calcd. H	Found C	Found H
IV	100	200	105	163–165 (d)	$C_{22}H_{17}N_5 \cdot HClO_4$	58.47	4.02	57.97	3.98
V	225	450	100	208 (d)	$C_{23}H_{19}N_5 \cdot HClO_4$	59.29	4.33	59.12	4.57
VI	100	180	110	189–190 (d)	$C_{23}H_{19}N_5 \cdot HClO_4$	59.29	4.33	58.95	3.96

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(6) J. Howitz and W. Schwenk, *Ber.*, **38**, 1282 (1905).

(7) All melting points are uncorrected. The microanalyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

TABLE III

ANALYTICAL AND OTHER DATA ON METAL COMPLEXES

Compound	Color	M.P., °C.	Formula	Calcd.				Found			
				C	H	N	Ni	C	H	N	Ni
IA	Black green	>300	$C_{23}H_{15}O_2N_5Ni$				12.98				13.43
IIA	Dark green	>300	$C_{24}H_{17}O_2N_5Ni$			15.02				14.89	
IIIA	Dark green	>300	$C_{24}H_{17}O_2N_5Ni$	61.83	3.68			60.83	3.86		
IB	Dark red	>330	$C_{23}H_{15}O_4N_5U$	41.63	2.28	10.56		39.96	2.79	9.90	
IIB	Dark red	236–237 (d)	$C_{48}H_{36}O_6N_{10}U$	53.03	3.34	12.89		52.99	3.53	13.36	
IIIB	Dark red	232–233 (d)	$C_{48}H_{36}O_6N_{10}U$	53.03	3.34	12.89		52.72	3.51	13.69	
VA	Dark green	263–264 (d)	$C_{23}H_{19}N_5 \cdot CoCl_2$	55.77	3.87	14.14		55.93	3.92	14.30	
VIA	Dark green	265 (d)	$C_{23}H_{19}N_5 \cdot CoCl_2$	55.77	3.87	14.14		56.12	4.20	14.36	

Nickel complexes (IA–IIIA). An alcoholic solution of 50 mg. of I was treated with a concentrated aqueous solution of 50 mg. nickel sulfate and of 50 mg. sodium acetate. The deep green solution was concentrated somewhat, the microcrystals which separated after cooling were sucked dry and rewashed thoroughly with water and then alcohol.

The other nickel complexes (Table III) were prepared similarly.

Uranyl complex (IB). An alcoholic solution of 50 mg. of I and 50 mg. uranyl acetate was heated on a waterbath under reflux for an hour and allowed to stand overnight. On the next day, the crystals which had separated were filtered and thoroughly washed with alcohol (Table III).

Uranyl complexes (IIB and IIIB). A warm alcoholic solution of 50 mg. compound II and 50 mg. uranyl acetate were brought together; the uranyl complex precipitated immediately and was recrystallized from alcohol. The complex IIIB was prepared analogously (Table III).

Cobalt complexes (VA and VIA). An alcoholic solution of 100 mg. of compound V and 65 mg. $CoCl_2 \cdot 6H_2O$ was heated on a water bath for about 0.25 hr. Crystals which separated were filtered and washed with alcohol. The complex VIA was prepared in the same way (Table III).

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