be possible to isolate the analogue free from carrier. It must be borne in mind, however, that at the present time these compounds are formed in quantities too small for practicable separation.

Investigations on the chemical fate of a recoiling carbon-14 atom are being carried out. It is hoped that the increasing amount of research in this field will provide accurate data for the correlation of re-entry versus total carbon-14 production in a given system. In addition, the method may become a valuable synthetic tool for the organic chemist.

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Steric Effects in the Formation of Copper and Cobalt Complexes with the Epimeric Salicylidenementhylamines

IN a previous communication[1], it was reported that cobaltous ions do not react readily with salicylidene-aniline bases bearing ortho substituents on the aniline ring. In the present communication are reported some further attempts to prepare similar complexes of cobalt and copper, using as the amine components of the salicylidene bases four epimeric forms of menthylamine which, with bulky *iso*propyl substituents and nonplanar ring forms, may be expected to exert considerable steric resistance to a tetrahedral grouping of ligands about cobalt ions. The complexes were prepared by mixing aqueous solutions of the metal acetates with an alcoholic solution of the salicylidene base[2]. The results of this work are indicated in Table 1, the complexes isolated being of the form *bis* (salicylidenementhylamine) cobalt (copper).

Table 1

Amine component	Co	Cu
Cyclohexylamine	+	+
(−)-Menthylamine	+	+
(+)-*neo*Menthylamine	−	−
(+)-*iso*Menthylamine	0	+
(±)-*neoiso*Menthylamine	0	+

+ = isolation of the complex *bis* (salicylideneamine) *M*.
− = no reaction: formation of metal hydroxide and unchanged Schiff's base.
0 = formation of oils or tar and unchanged Schiff's base.

The inability of salicylidene-(+)-*neo*menthylamine to form complexes with either cobalt or copper points to a strong steric hindrance with respect to both the nitrogen atom and the phenolic hydroxyl in this case. (−)-Menthylamine and (+)-*neo*menthylamine differ only in the configuration of the amino-group at $C_{(3)}$, and the ready formation of complexes with (−)-menthylamine (with both copper and cobalt) is explainable on the basis of this relationship. A consideration of the probable conformations of strainless rings for the amines[3,4] suggests that the *cyclo*hexane ring contributes considerably to the steric hindrance preventing complex formation with (+)-*neo*menthylamine, in which the amino-group occupies an axial position, whereas no such effect impedes complex formation with (−)-menthylamine, which has an equatorial amino-group.

With copper and salicylidene-(+)-*iso*menthylamine the expected complex was isolated as readily as in the case of (−)-menthylamine; but with cobalt the reaction produced only a reddish tar together with unchanged base, and no solid complex could be isolated from the mixture. It is not immediately obvious why cobalt does not form a derivative with the (+)-*iso*menthylamine base while copper does, even on the assumption of a tetrahedral arrangement for the expected cobalt complex. This difference observed between the behaviour of salicylidene-(−)-menthylamine and that of salicylidene-(+)-*iso*menthylamine towards cobalt ions was not expected, as the difference between the two amines is believed to be only in the position of the methyl group (1*e* in the case of menthylamine and 1*p* in *iso*menthylamine[4]).

Although no complex could be obtained with cobalt and salicylidene-(±)-*neoiso*menthylamine, but only a reddish tar and unchanged Schiff's base, the copper derivative, on the other hand, was readily isolated. The lesser hindrance towards complex formation of (±)-*neoiso*menthylamine compared with that of (+)-*neo*menthylamine is in agreement with the greater reactivity of *neoiso*menthol over that of *neo*menthol towards acid chlorides[5]. If the inability of salicylidene-(+)-*neo*menthylamine to form complexes with both copper and cobalt ions is due chiefly to the spatial arrangement of the *iso*propyl and amino-groups, it seems unlikely that *neoiso*menthylamine has, in these reactions at least, a conformation in which the amino-group occupies an axial position. Rather, our results tend to support the view that *neoiso*menthyl derivatives are examples of conformational instability (Mills, J. A., private communication), and that it is possible for the amino-group in *neoiso*menthylamine to adopt an equatorial position[3].

Relative pK_a values have been determined for the four menthylamine epimers by potentiometric titration in 50 per cent aqueous ethanol against hydrochloric acid. As can be seen from Table 2, the order of decreasing basic strength is *iso*menthylamine, menthylamine, *neo*menthylamine, and *neoiso*menthylamine.

The apparent non-reactivity of several of the salicylidene-menthylamine bases with cobalt, and of the *neo*menthylamine derivative with copper and cobalt cannot be ascribed to differences in the basicities of the amines. They are all comparably strong bases, and the electron density on the nitrogen atom in each case should not differ greatly throughout the series. Steric effects related to the tendency to form planar (copper) or tetrahedral (cobalt) derivatives as outlined above seem to provide the only

Table 2. pK_a VALUES OF FOUR EPIMERIC MENTHYLAMINES DETERMINED IN 50 PER CENT AQUEOUS ETHANOL AT 20°

	pK_a
(+)-*iso*Menthylamine	9·93
(−)-Menthylamine	9·73
(+)-*neo*Menthylamine	9·69
(−)-*neoiso*Menthylamine	9·47

other explanation of the difference in reactivity between copper and cobalt with the various bases studied.

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Crystallization of Silver Chromate

The precipitation of silver chromate from its supersaturated solutions has been studied by van Hook[1], who concluded that crystallization could be represented as a two-step process: first, an induction period varying inversely with the volume of seed suspension used, during which the principal action was the generation of crystal nuclei; secondly, a bimolecular growth of these nuclei.

It is well known that the inoculation of supersaturated solutions with seed crystals results in the growth of these added crystals rather than the formation of crystal nuclei[2]. Crystallization of silver chloride begins immediately on seeding a supersaturated solution. Delayed crystallization, however, similar to that reported by van Hook, is encountered when seed suspensions are aged before use in the presence of suitable poisoning substances such as eosine[3]. The observed inverse relationship between the duration of these induction periods and the volumes of poisoned suspension used suggests that the results of van Hook were due to the presence of adsorbed contaminant at the surface of aged silver chromate crystals. The present work was designed to test this suggestion.

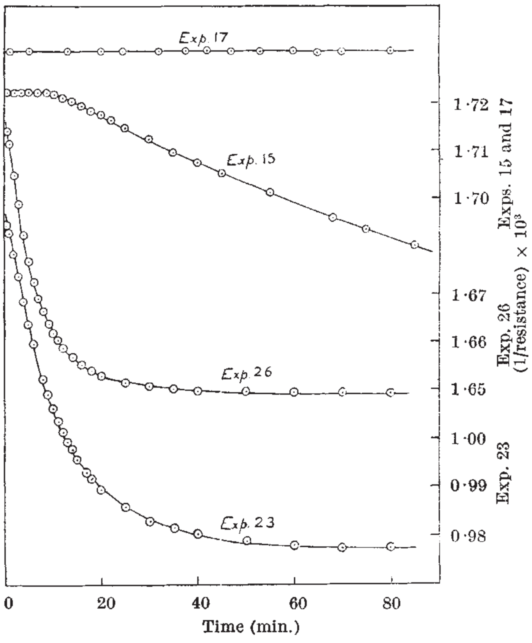

Fig. 1. Time plots of the reciprocal of the resistance of the solution

Preliminary experiments confirmed the existence of a well-defined critical supersaturation: it was possible to prepare stable solutions of silver chromate in which the molar concentration product $[\mathrm{Ag}^+]^2[\mathrm{CrO}_4^{=}]$ exceeded the solubility value by more than 300 per cent. The solubility of silver chromate at 25° was determined by the equilibration (*a*) of pure solid with conductivity water ($0 \cdot 923 \times 10^{-4}$ moles/l.), and (*b*) of highly supersaturated solutions ($0 \cdot 931 \times 10^{-4}$ moles/l.).

Crystallization experiments were carried out at 25° using the conductivity technique described elsewhere[3]. Supersaturated solutions of silver chromate were prepared in a stirred conductivity cell by mixing silver nitrate and potassium chromate solutions, and crystallization was induced by the addition of a small volume, usually 5 ml., of the appropriate seed suspension. Some typical results are shown in Fig. 1, in which the reciprocal of the resistance of the solution (a measure of the extent of crystallization) is plotted against time.

Solubility product = $3 \cdot 186 \times 10^{-12}$

Experiment	Initial concentrations moles/l. × 10^4 $[\mathrm{Ag}^+]$	Initial concentrations moles/l. × 10^4 $[\mathrm{CrO}_4^{=}]$	$[\mathrm{Ag}^+]^2[\mathrm{CrO}_4^{=}]$ × 10^{12}
15	2·234	1·129	5·635
17	2·250	1·130	5·720
23	2·254	1·127	5·726
24	3·580	0·448	5·725
26	1·420	2·840	5·727

An aged seed suspension, prepared by crystallization from boiling saturated silver chromate solution, was used in Exp. **17** and no change in conductivity was detected for at least four hours, even though a sensible supersaturation persisted. Thorough washing of this aged suspension with boiling conductivity water before use in Exp. 15 resulted in a substantial reduction in the time of induction. In Exps. 23, 24 and 26, the use of freshly precipitated seed suspension of available growth area less than half that of the aged suspension enabled crystallization to start immediately on seeding. These results provide conclusive evidence that any induction effect is due to contamination of the surface of aged crystals. Hydrolysis products, the most likely contaminants, might include any or all of the species HCrO_4^-, AgOH, $\mathrm{Ag}_2\mathrm{OH}^+$.

It is seen from Fig. 2 that the rate of crystallization, $-\,\mathrm{d}m/\mathrm{d}t$ (moles.l.$^{-1}$min.$^{-1}$), obtained from the curves in Fig. 1, is best interpreted in terms of third-order

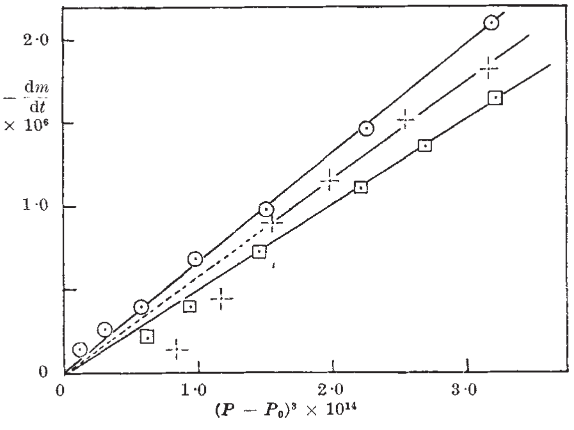

Fig. 2. Third-order kinetic plot. Exp. 23, ⊙ ; exp. 26, + exp. 24, ⊡