Reactions of Aquo-complexes of Cobalt(III) with Acylating Reagents

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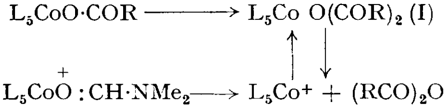
THE synthesis of carboxylato-complexes of cobalt(III) (*e.g.* $L_5CoOCOR$) is generally effected by substitution of the corresponding aquo-complex;[1] though widely successful,[1,2] this method has failed for several potentially interesting complexes.[1,2] Such failures have been attributed to a competitive decomposition of the ligand[3] or aquo-complex.[4] The reaction of chloro-complexes with silver carboxylates has also been used.[5] An alternative general method, *viz.* one involving direct acylation, appeared feasible since, in 1907, Werner[6] reported the formation of acetato- and propionato-pentamminecobalt(III) nitrate by trituration of the hydroxopentammine salt with acetic and propionic anhydrides, respectively. We now report a study of the acylation of aquo-complexes of cobalt(III) including general methods for the preparation of carboxylato-complexes in high yields by a reaction which proceeds rapidly and stereospecifically under very mild conditions.

A solution of the aquo-complex in dimethylformamide (DMF) is treated at room temperature with a slight excess of the acid anhydride and two to three mol. equivalents of *NN*-dimethylbenzylamine. Complete reaction is immediate, as judged by the colour change in the solutions. In cases where the acid anhydrides were not available they were prepared, *in situ*, from the acids and dicyclohexylcarbodi-imide[7] or by the interaction of the acid chloride with the corresponding silver salt of the acid. By this method, aquo-pentamminecobalt(III) perchlorate was converted to the corresponding acetato-,[8] benzoato-,[9] hydrogen maleato-,[10] sorbato-[9] and pivalato-[11] complexes in high yields. Even the reaction with the sterically hindered pivalic anhydride was immediate. That the reaction is stereospecific is indicated by the conversion of *cis*- and *trans*-$[Co(en)_2(OH_2)_2](NO_3)_3$ to *cis*-$[Co(en)_2(OCOMe)_2]CH_3COO$ and *trans*-$[Co(en)_2(OCOMe)_2]NO_3$, respectively.[12]† It is envisaged that the role of the tertiary base is to generate a kinetically significant concentration of hydroxo-complex, since in the absence of the base reaction is very slow. Indeed we have confirmed Werner's observation[6] and have shown that the hydroxopentammine complex also reacts rapidly in dimethylformamide solution.

Other solvents may be used: thus dimethyl sulphoxide is a suitable solvent and, furthermore, crystalline acetatoperchlorate of analytical purity is produced in 93% yield merely by leaving the aquo-complex in water with a slight excess of ammonia and three equivalents of acetic anhydride. Even the type of acylating agent can be varied. For instance, acetylation by 4-nitro- or 2,4-dinitrophenyl acetate proceeds cleanly in dimethylformamide.

Because of the reactivity and availability, acid chlorides were suggested as acylating reagents for aquo-complexes. However, attempts to use acid chlorides to acylate $[Co(NH_3)_5OH_2](ClO_4)_3$ were frustrated by the immediate precipitation of the chloride salt. In an attempt to circumvent this difficulty, the use of acetyl perchlorate was examined. In the absence of base this reagent gave a quantitative yield of *NN*-dimethylformamidopentamminecobalt(III),[2] a reaction which in fact constitutes an excellent method of preparing the DMF complex. This product also results if the acetato-complex is treated in the same way. Control experiments showed that the DMF complex does not arise from solvolysis of either the aquo- or acetato-complex. Addition of *NN*-dimethylbenzylamine (slight excess over acetyl perchlorate) completely represses the formation of the DMF complex and under these conditions the aquo-complex is converted into the acetato-complex. This method is however less suitable for unsaturated acids, the acylium ions of which are less stable. The mechanism of the formation of the dimethylformamido-complex probably involves the following scheme.



$$\begin{tikzcd}
L_5CoO{\cdot}COR \arrow[r, "R\overset{+}{C}O"] & L_5Co\,\overset{+}{O}(COR)_2\ (I) \arrow[d, shift left] \\
L_5Co\overset{+}{O}:CH{\cdot}NMe_2 \arrow[r] & L_5Co^+ + (RCO)_2O \arrow[u, shift left]
\end{tikzcd}$$

Since acid anhydrides will be very weakly nucleophilic ligands, complexes of the type (I) are expected to be potentially useful precursors of a variety of co-ordination complexes. Thus, treatment of a solution of benzoatopentamminecobalt(III) in trimethyl phosphate with silver perchlorate and benzoyl chloride yielded the

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† The stereochemical purity of the reactants and products was conveniently established by n.m.r. spectroscopy to be 100% (accuracy of 1%).

corresponding trimethyl phosphato-complex (λ_{max} 520 mμ)[13] which in turn was converted into the acetato-complex by addition of acetic acid.

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