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The Halogenation and Nitration of the Optical Active Isomer of the *α*-Acetylacetonato(triethylenetetramine)cobalt(III) Complex

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Synopsis. The methylidyne hydrogen of the coordinated acetylacetonate ion in (+)$_D$-α-acetylacetonato(triethylenetetramine)cobalt(III) perchlorate has been replaced with halogens and with a nitro group with a complete retention of the configuration. The order of the molar rotations of the complexes has been found to be: acac-$<$Clacac-$<$Bracac-$<$Iacac-complex and acac-$\simeq$O$_2$Nacac-complex.*

Resolution into the optical-active antipodes from a synthesized metal complex is generally tedious, since we have no common knowledge as to a suitable resolving reagent for the specified complex. Therefore, if an active complex which has been resolved can be converted into its derivatives with a complete retention of the configuration, our labor in the preparation of the active complexes will be greatly reduced. This technique has been used for the preparation of some active complexes of cobalt(III).[1] However, when a substitution of a ligand is involved in the procedure, there is always a possibility of racemization during the reaction, and the verification of the optical purity of the product remains necessary.

We have found that (+)$_D$-[Co(acac)(en)$_2$]$^{2+}$* reacts with a slight excess of *N*-chlorosuccinimide in water and in a methanol(50%)–water mixture at *ca.* 40 °C with an increase in activity to form (+)$_D$-[Co(Clacac)(en)$_2$]$^{2+}$. The activity of the solution at t_∞ (practically, after 1 day) was the same as that of the solution with an equal concentration prepared with the isolated and recrystallized (+)$_D$-[Co(Clacac)(en)$_2$](ClO$_4$)$_2$. This means that the chlorination proceeds with a complete retention of the configuration under those conditions; accordingly, (+)$_D$-[Co(acac)(en)$_2$](ClO$_4$)$_2$ was treated with the other *N*-halogenosuccinimides and active halogenoacetylacetonato complexes have been obtained.[2] In order to make surer the halogenations with a retention of configuration, (+)$_D$-α-[Co(acac)(trien)](ClO$_4$)$_2$ was newly prepared and was treated with *N*-halogenosuccinimides. Furthermore, the nitration of the ligand in both active complexes was examined using a mixture of copper(II) nitrate trihydrate and acetic anhydride as a nitration reagent. Thus, a series of optically active halogenated and nitrated complexes were isolated as crystals.

Experimental

Preparation of (+)$_D$-α-[Co(acac)(trien)](ClO$_4$)$_2$. In 10 ml of water, 2.5 g of the racemic perchlorate salt and 1.0 g of potassium acetate were stirred for 10 min, and then the mixture was cooled. The precipitate(KClO$_4$) was filtered off. Into the filtrate, 1.3 g (1/2 equiv. to the complex) of (+)$_D$-NaAsOC$_4$H$_4$O$_6$ in 3 ml of water was added. Since it took a long time for the first crystal to come out, a few pieces of (+)$_D$-[Co(acac)(en)$_2$][(+)$_D$-AsOC$_4$H$_4$O$_6$]$_2$[3] were added to induce the crystal growth. Thus, pale red crystals came out gradually. After the mixture had been placed in a refrigerator overnight, the precipitate was separated and washed with ethanol and ether. Yield, 1.8 g.

Into a suspension of 0.5 g of the diastereoisomeric salt in 30 ml of ethanol, 3 ml of aqueous 2 M NaClO$_4$ was added. The mixture was then stirred vigorously for 1 h at *ca.* 45 °C, whereupon the solid phase turned white. The solid(NaAsOC$_4$H$_4$O$_6$) was subsequently filtered off, and the filtrate was evaporated to dryness. To the residue we added 5 ml of warm water, and, after the removal of a white insoluble material by filtration, a few drops of 6 M HClO$_4$ were added to the filtrate, which was then cooled. The bright red crystals which were thus precipitated were collected and washed with an ethanol(20%)–ether mixture and with ether. Yield, 0.3 g.

Preparation of (+)$_D$-[Co(acac)(en)$_2$](ClO$_4$)$_2$. The procedure of the preparation was described in the preceding report.[2]

Chlorination, Bromination, Iodination, and Nitration of the Active Complexes. The halogenations and the nitration of the active isomers were carried out by the methods used for the inactive complexes.[2]

Identification and Measurement of the Optical Rotations. Each complex was identified by making sure its absorption spectrum was identical with that of the respective inactive complex.[2] The rotation of the complexes was counted with a JASCO DIP 180 Polarimeter at 589, 577, 546, 435, and 405 nm, using a 0.1% aqueous solution for the first four wavelengths and a 0.02% solution for the last wavelength.

Results and Discussion

Sodium arsinyl tartrate, which is known as an excellent resolving reagent for [Co(acac)(en)$_2$]$^{2+}$,[3] is also useful for the resolution of α-[Co(acac)(trien)]$^{2+}$. The conversion of the diastereoisomeric salt into the perchlorate was carried out by utilizing the property of the perchlorate of being soluble in ethanol including a small amount of water.

The molar rotations of the obtained complexes are shown in Table 1. As may be seen in the table, the rotatory characters of the trien complexes as well as of the en complexes are quite similar to each other; therefore, the chirality around the central cobalt must be same, and, since (+)$_D$-[Co(acac)(en)$_2$]$^{2+}$ has been established as having the Λ-configuration,[4] all of the trien complexes as well as the halogenated and nitrated en complexes can be concluded as having the Λ-configuration:

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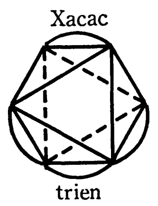
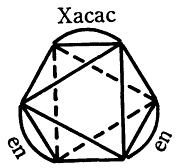
* The following abbreviations have been used in this report: en, ethylenediamine; trien, triethylenetetramine; acac, acetylacetonate ion (2,4-pentanedionate ion); Clacac, chloroacetylacetonate ion (3-chloro-2,4-pentanedionate ion); Bracac, bromoacetylacetonate ion; Iacac, iodoacetylacetonate ion; O$_2$Nacac, nitroacetylacetonate ion.

TABLE 1. MOLAR ROTATIONS OF $(+)_D$-[Co(Xacac)(en)$_2$]-(ClO$_4$)$_2$ AND $(+)_D$-α-[Co(Xacac)(trien)](ClO$_4$)$_2$

Complex	[M]$_{589}$	[M]$_{577}$	[M]$_{546}$	[M]$_{435}$	[M]$_{405}$
$(+)_D$-[Co(Xacac)(en)$_2$](ClO$_4$)$_2$					
acac	+2280°	+2900°	+3200°	−11500°	−11800°
Clacac	+2590°	+3260°	+3330°	−12700°	−13300°
Bracac	+2630°	+3280°	+3340°	−12800°	−13600°
Iacac	+2770°	+3330°	+3410°	−13500°	−14400°
O$_2$Nacac	+2090°	+2650°	+3750°	−11500°	−12600°
$(+)_D$-α-[Co(Xacac)(trien)](ClO$_4$)$_2$					
acac	+2560°	+3280°	+4630°	−13700°	−13500°
Clacac	+3130°	+3900°	+4990°	−16000°	−15800°
Bracac	+3210°	+4060°	+5270°	−16800°	−16200°
Iacac	+3330°	+4200°	+5350°	−17800°	−16700°
O$_2$Nacac	+2240°	+2840°	+5050°	−15300°	−14600°



$(+)_D$-α-[Co(Xacac)(trien)]$^{2+}$



$(+)_D$-[Co(Xacac)(en)$_2$]$^{2+}$

The orders of the activities can be seen as:

acac-$<$Clacac-$<$Bracac-$<$Iacac-complex

and

acac-$\simeq$O$_2$Nacac-complex

in both en and trien complexes. Thus, the increase or the maintenance of rotation by the substitutions indicates that the reactions proceed without any bond rupture between the cobalt and the ligands, as has been verified in the chlorination of [Co(acac)(en)$_2$]$^{2+}$; hence, the method for obtaining these optical active isomers has been greatly simplified.

References

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