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BROMINATION AND NITRATION OF SOME MIXED LIGAND ACETYLACETONATOCOBALT(III) COMPLEXES

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Four kinds of mixed ligand acetylacetonatocobalt(III) complexes (($(NH_3)_4$-, $(en)_2$-, α-trien-, and β-trien-complexes) have been substituted with bromine, and five (the above four and fac(N)-i-DTMA-complex) have been substituted with nitro group at the central methine of the ligand. The brominated and the nitrated complexes have been isolated and identified by means of the electronic absorption spectra and the NMR spectra.

Collman and his group investigated extensively various electrophilic substitutions such as halogenation, nitration, and acetylation, at the central methine of the ligand in the acetylacetonatometal complexes.[1-3] However, the complexes studied by them are mostly the tris(acetylacetonato)metal(III) or bis(acetylacetonato)metal(II), which are neutral and soluble in organic solvents. Only a few papers report that mixed ligand acetylacetonatometal complexes have been substituted at the methine by the electrophiles.[4] It has also been reported that the acetylacetonatobis(ethylenediamine)cobalt(III) ion, $[Co(acac)(en)_2]^{2+}$, is not brominated even under forcing conditions.[5] We succeeded recently in the bromination of fac(N)- and mer(N)-$[Co(acac)(i\text{-}DTMA)]ClO_4$ (i-DTMA = 4-diethylenetriaminemonoacetate ion) with N-bromosuccinimide in ethanol(50%)-water mixture.[6] Continuing that study, we found that the bromination and the nitration were accomplished without difficulty in several kinds of cationic mixed ligand acetylacetonatocobalt(III) complexes. This report deals with the preparation and the identification of the substituted complexes.

Preparation. 1) Bromoacetylacetonatobis(ethylenediamine)cobalt(III) Perchlorate, $[Co(Bracac)(en)_2](ClO_4)_2$. Carbonatobis(ethylenediamine)cobalt(III) perchlorate (2.7 g) was dissolved in 8 ml of 2M $HClO_4$. To this solution was added a solution of acetylacetone (1.6 ml) in 12 ml of 1M NaOH. The mixture was stirred at ~70°C for 2 hr and then was concentrated to ~5 ml. The dark red solution became

Table 1. Results of Elemental Analyses of the Complexes.

Complex	C,Found9)(Calcd)	H,Found9)(Calcd)	N,Found9)(Calcd)
$[Co(Bracac)(NH_3)_4](ClO_4)_2$	11.91 (11.92)	3.77 (3.60)	11.11 (11.12)
$[Co(O_2Nacac)(NH_3)_4](ClO_4)_2$	12.96 (12.78)	4.15 (3.86)	14.96 (14.90)
$[Co(Bracac)(en)_2](ClO_4)_2$	19.82 (19.44)	4.15 (3.99)	10.29 (10.08)
$[Co(O_2Nacac)(en)_2](ClO_4)_2 \cdot H_2O$	20.02 (20.01)	4.57 (4.48)	12.95 (12.97)
α-$[Co(Bracac)(trien)](ClO_4)_2$	22.92 (22.70)	4.28 (4.16)	9.69 (9.63)
α-$[Co(O_2Nacac)(trien)](ClO_4)_2$	24.10 (24.10)	4.45 (4.41)	12.81 (12.78)
β-$[Co(Bracac)(trien)](ClO_4)_2$	22.74 (22.70)	4.21 (4.16)	9.62 (9.63)
β-$[Co(O_2Nacac)(trien)](ClO_4)_2 \cdot H_2O$	23.34 (23.33)	4.48 (4.63)	12.38 (12.37)
fac(*N*)-$[Co(O_2Nacac)(i\text{-}DTMA)]ClO_4$	28.55 (28.56)	4.54 (4.36)	11.85 (12.11)

muddy upon cooling. The solid collected on a filter was extracted with 10 ml of methanol. By the slow evaporation of the solvent from the extract, a large amount of red crystals came out, which was collected and washed with a methanol(20%)-ether mixture and then with ether. Yield, 2.5 g. By the addition of sodium iodide to the combined filtrate of the above procedure, the complex can be recovered as the iodide salt.

A solution of $[Co(acac)(en)_2](ClO_4)_2$ obtained above (2.4 g) in 20 ml of water was mixed with a solution of *N*-bromosuccinimide (1.0 g) in 15 ml of acetone. The mixture was stirred at ~50°C for 30 min and then was concentrated to ~15 ml at the temperature. After cooling the solution, 0.5 ml of 6M $HClO_4$ was added; the red precipitate formed was recrystallized from 10 ml of water (~60°C) with the addition of a few drops of 6M $HClO_4$. The product was washed with ethanol and ether. Yield, 1.5 g (53%).

2) Nitroacetylacetonatobis(ethylenediamine)cobalt(III) Perchlorate Monohydrate, $[Co(O_2Nacac)(en)_2](ClO_4)_2 \cdot H_2O$. The preparation was carried out in a way similar to Collman's method for the nitration of $[Co(acac)_3]$.7) Finely devided copper(II) nitrate trihydrate (0.7 g) was mixed into 60 ml of acetic anhydride at 0°C and the mixture was stirred for 15 min. Into this mixture was added 1.2 g of $[Co(acac)(en)_2](ClO_4)_2$. The mixture was stirred at 0°C for 1 hr and then at the room temperature for another hour. The bluish product thus obtained was poured into ice(90 g)-water(90 g). The two-liquid-phase mixture was stirred until it became homogeneous and reddish brown (~1 hr). The solution was then concentrated to ~15 ml in a rotary evaporator below 60°C. A brown-red precipitate came out by the addition of 1 ml of 6M $HClO_4$ and upon cooling. It was recrystallized from 10 ml of water (~60°C) with the addition of a few drops of 6M $HClO_4$. Yield, 0.6 g (44%).

3) Other Complexes. The other complexes in Table 1 (except for the last one) were derived as the above preparations from the carbonato complexes ($[CoCO_3(NH_3)_4]ClO_4$, α-$[CoCO_3(trien)]ClO_4$,8) and β-$[CoCO_3(trien)]ClO_4$8)). The last complex was derived by

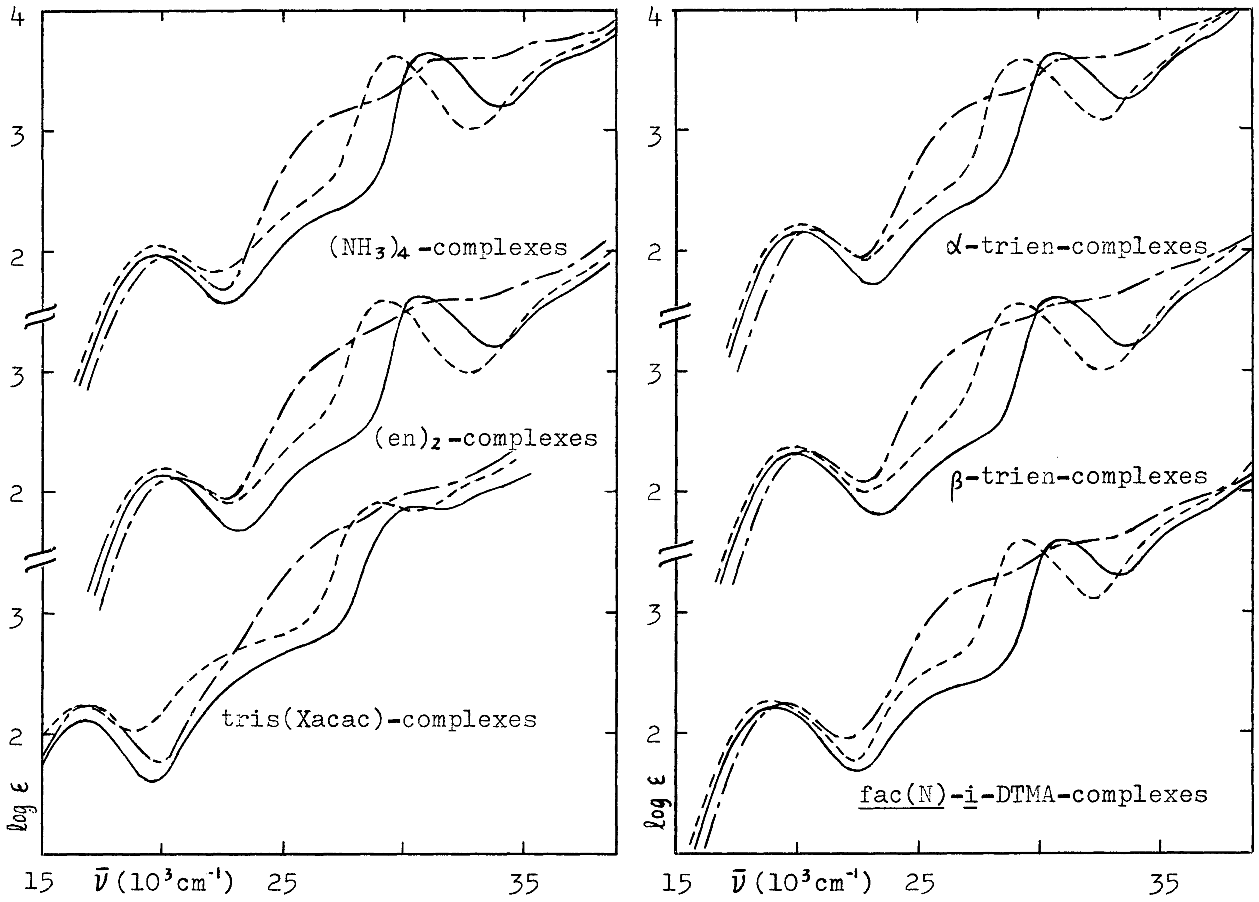

Fig. 1. Electronic Absorption Spectra.

——— : unsubstituted complex, ----- : brominated complex, —·—·—: nitrated complex

nitrating fac(N)-[Co(acac)(i-DTMA)]ClO_4[6] as in 2). The bromination of fac(N)- and mer(N)-[Co(acac)(i-DTMA)]ClO_4 was reported previously.[6] The brominated and the nitrated species of [$Co(acac)_3$] were prepared by Collman's method.[2,7]

Identification. The electronic absorption spectra of the complexes prepared are shown in Fig. 1. Since the bromination and the nitration of [$Co(acac)_3$] have been well-established, the spectral variations observed between the spectrum of [$Co(acac)_3$] and that of [$Co(Bracac)_3$] or [$Co(O_2Nacac)_3$] may be adopted as an indication of the bromination or the nitration at the methine of the ligand. As may be seen in Fig. 1, the specific band arising around $30 \times 10^3 cm^{-1}$ (which has been assigned to the transition of an electron from the metal t_{2g} to the ligand π^* orbital[10]) shifts to a lower wave number by bromination, while the band expands with a considerable deformation of the band feature by nitration. (The expansion and deformation probably arises from an overlap of the absorption of the nitro group onto the $\pi^* \leftarrow t_{2g}$ band.) These spectral variations are also found in the spectra of the mixed ligand complexes reported here, and support our formulations.

The NMR spectra have also indicated the substitutions: The resonances due to the methine hydrogen observed around 4.5 ppm (referred to tert-butanol as zero) in the spectra of the unsubstituted complexes disappeared in those of the substituted species.

Notes on the Preparations. Acetylacetonatobis(ethylenediamine)cobalt(III) is usually obtained as the iodide salt owing to the easiness of the isolation.[11] The bromination of the iodide was also attempted. However, a redox reaction appeared to occur simultaneously, and the product was too complicated to isolate the brominated species. The perchlorate is more soluble in water than the iodide, and is very soluble in methanol, ethanol, and acetone, especially when it is wet. Therefore, the perchlorate is a little difficult to handle in its preparation. However, it is rather suitable for the substitutions, and no trouble was found in its bromination and nitration. A more or less similar situation was observed in the other acetylacetonato complexes. The only ill success of the nitration in mer(N)-[Co(acac)(i-DTMA)]ClO_4 is due to its insolubility into the nitration reagent. It has been argued that, because of the electrostatic interaction between the substrates and the electrophiles, cationic acetylacetonatometal complexes are more resistant against electrophilic substitutions at the methine than neutral and anionic complexes.[4] However, our result indicates that this is not necessarily true. The ill success in the bromination of $[Co(acac)(en)_2]^{2+}$ by Collman's group,[5] although the detail of their procedure is not available to us, is supposed to be simply due to an unsuitable counter anion.

References and Footnotes:

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