September, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (9), 2445—2450 (1976) 2445

Halogenation and Nitration of Some Mixed Ligand Acetylacetonatocobalt(III) Complexes

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(Received December 2, 1975)

In six kinds of mixed ligand acetylacetonatocobalt(III) complexes ((NH$_3$)$_4$-, (en)$_2$-, α-trien-, β-trien-, *fac(N)-i*-dtma-, and *mer(N)-i*-dtma-complexes†), the methine hydrogen of the coordinated acetylacetonate ion has been substituted with chlorine, bromine, and iodine, and in five of them excepting the *mer(N)-i*-dtma complex, it has been substituted with a nitro group. The halogenated and the nitrated complexes were isolated and identified by means of electronic absorption spectra and NMR spectra. The effects of the substitutions on the properties and the characteristics of the substitution reactions are described and discussed.

Collman and his collaborators have investigated extensively various electrophilic substitutions, such as halogenation, nitration, and acetylation at the central methine of the ligand in acetylacetonatometal complexes.[1] *N*-Halogenosuccinimides have been found to be excellent reagents for halogenation,[2] and a mixture of copper(II) nitrate and acetic anhydride for nitration.[3] However, the complexes they studied are mostly tris(acetylacetonato)metal(III) or bis(acetylacetonato)metal(II), which are neutral and soluble in organic solvents. Only a few papers have reported that mixed ligand acetylacetonatometal complexes were substituted at the methine by electrophiles.[4] It has also been reported that the acetylacetonatobis(ethylenediamine)cobalt(III) ion, [Co(acac)(en)$_2$]$^{2+}$, is not brominated even under forced conditions.[5] The present authors have recently succeeded in the bromination of *fac*(*N*)- and *mer*(*N*)-[Co(acac)(*i*-dtma)]ClO$_4$† with *N*-bromosuccinimide in a ethanol(50%)–water mixture.[6] Therefore, it was thought worthwhile to further examine these substitutions, using the other kinds of mixed ligand acetylacetonatocobalt(III) complexes, especially those with high positive charges. As a result, the halogenation and the nitration were accomplished without difficulty in several kinds of the cationic complexes. This report deals with the preparation and characterization of the substituted complexes and a preliminary consideration of the substitution mechanism.

Experimental

Materials, Analysis, Apparatus, and Measurements. All the chemicals used were of the reagent grade and were used without further purification. The carbon, hydrogen, and nitrogen in the synthesized complexes were analyzed by the Analytical Center of the Institute for Chemical Research of Kyoto University. The visible and ultraviolet absorption spectra were measured in aqueous solution with a Hitachi EPS-3T Recording Spectrophotometer. The optical rotations were counted with a JASCO DIP-180 Polarimeter at 589 and 405 nm. The proton NMR spectra were recorded with a Japan Electron Optics JNM-100 Spectrometer (100 MHz), using deuterium oxide as the solvent and *t*-butanol as the internal reference. The temperature of the probe was maintained at 22±1 °C.

Chlorination, Bromination, and Iodination. The halogenations were carried out using *N*-halogenosuccinimides in methanol(50%)–water or acetone(50%)–water mixtures at *ca.* 50 °C. Since the procedures of the halogenation for each acetylacetonato complex were quite similar, only a representative case will be described below.

A solution of [Co(acac)(en)$_2$](ClO$_4$)$_2$[7] (2.4 g) in 15 ml of water was mixed with a solution of *N*-chlorosuccinimide (0.8 g) in 15 ml of acetone. The mixture was stirred at *ca.* 50 °C for 30 min, and was then concentrated to *ca.* 10 ml at that temperature. A red precipitate resulted upon the addition of 1 ml of 6 M HClO$_4$ with cooling. The precipitate was recrystallized with 10 ml of warm water and the addition of a few drops of 6 M HClO$_4$. The product was washed with ethanol and ether. Yield, 1.5 g.

Nitration. The nitration was carried out in a manner similar to Collman's method for the nitration of [Co(acac)$_3$].[8] Again, since the procedures for each complex were quite similar, only a representative case will be described.

Finely divided 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 the mixture was added 1.2 g of [Co(acac)(en)$_2$](ClO$_4$)$_2$. The mixture was stirred at 0 °C for 1 h and then at room temperature for another hour. The bluish product thus obtained was poured into an ice(90 g)–water (90 g) mixture. The double liquid mixture was stirred until it became homogeneous and reddish brown (*ca.* 1 h). The solution was then concentrated to *ca.* 15 ml in a rotary evaporator below 60 °C. A brown-red precipitate resulted upon the addition of 1 ml of 6 M HClO$_4$ followed by cooling. It was recrystallized with 10 ml of warm water and the addition of a few drops of 6M HClO$_4$. The product was washed with ethanol and ether. Yield, 0.6 g.

Six kinds of mixed ligand acetylacetonatocobalt(III) complexes ([Co(acac)(NH$_3$)$_4$](ClO$_4$)$_2$,[7] [Co(acac)(en)$_2$](ClO$_4$)$_2$, α-[Co(acac)(trien)](ClO$_4$)$_2$,[7] β-[Co(acac)(trien)]Br$_2$,[7] *fac(N)*-[Co(acac)(*i*-dtma)]ClO$_4$,[6] and *mer(N)*-[Co(acac)(*i*-dtma)]ClO$_4$[6]) were attempted for their chlorination, bromination, iodination, and nitration in manners similar to that described above, and all but the nitration of *mer(N)*-[Co-

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† The following abbreviations are used in this article: en, ethylenediamine; trien, triethylenetetramine; *i*-dtma, bis(2-aminoethyl)aminoacetate ion (4-diethylenetriaminemonoacetate ion); 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. Results of elemental analysis of the complexes

Complex	Composition	F.W.	Found (%)			Calcd (%)		
			C	H	N	C	H	N
$[Co(Clacac)(NH_3)_4](ClO_4)_2$	$CoC_5H_{18}O_{10}N_4Cl_3$	459.51	12.88	4.28	12.14	13.07	3.95	12.19
$[Co(Bracac)(NH_3)_4](ClO_4)_2$	$CoC_5H_{18}O_{10}N_4Cl_2Br$	503.96	11.91	3.77	11.11	11.92	3.60	11.12
$[Co(Iacac)(NH_3)_4](ClO_4)_2 \cdot H_2O$	$CoC_5H_{20}O_{11}N_4Cl_2I$	568.98	10.61	3.97	9.97	10.55	3.54	9.85
$[Co(O_2Nacac)(NH_3)_4](ClO_4)_2$	$CoC_5H_{18}O_{12}N_5Cl_2$	470.07	12.96	4.15	14.96	12.78	3.86	14.90
$[Co(Clacac)(en)_2](ClO_4)_2$	$CoC_9H_{22}O_{10}N_4Cl_3$	511.59	21.02	4.56	10.87	21.13	4.34	10.95
$[Co(Bracac)(en)_2](ClO_4)_2$	$CoC_9H_{22}O_{10}N_4Cl_2Br$	556.04	19.82	4.15	10.29	19.44	3.99	10.08
$[Co(Iacac)(en)_2](ClO_4)_2$	$CoC_9H_{22}O_{10}N_4Cl_2I$	603.04	17.76	3.79	9.18	17.93	3.68	9.29
$[Co(O_2Nacac)(en)_2](ClO_4)_2 \cdot H_2O$	$CoC_9H_{24}O_{13}N_5Cl_2$	540.16	20.02	4.57	12.95	20.01	4.48	12.97
α-$[Co(Clacac)(trien)](ClO_4)_2$	$CoC_{11}H_{24}O_{10}N_4Cl_3$	537.63	24.32	4.41	10.27	24.57	4.50	10.42
α-$[Co(Bracac)(trien)](ClO_4)_2$	$CoC_{11}H_{24}O_{10}N_4Cl_2Br$	582.08	22.92	4.28	9.69	22.70	4.16	9.63
α-$[Co(Iacac)(trien)](ClO_4)_2$	$CoC_{11}H_{24}O_{10}N_4Cl_2I$	629.08	20.79	3.93	8.77	21.00	3.85	8.91
α-$[Co(O_2Nacac)(trien)](ClO_4)_2$	$CoC_{11}H_{24}O_{12}N_5Cl_2$	548.18	24.10	4.45	12.81	24.10	4.41	12.78
β-$[Co(Clacac)(trien)](ClO_4)_2 \cdot H_2O$	$CoC_{11}H_{26}O_{11}N_4Cl_3$	555.64	23.39	4.77	9.95	23.78	4.71	10.08
β-$[Co(Bracac)(trien)](ClO_4)_2$	$CoC_{11}H_{24}O_{10}N_4Cl_2Br$	582.08	22.74	4.21	9.62	22.70	4.16	9.63
β-$[Co(Iacac)(trien)](ClO_4)_2$	$CoC_{11}H_{24}O_{10}N_4Cl_2I$	629.08	20.92	3.96	8.87	21.00	3.85	8.91
β-$[Co(O_2Nacac)(trien)](ClO_4)_2 \cdot H_2O$	$CoC_{11}H_{26}O_{13}N_5Cl_2$	566.19	23.34	4.48	12.38	23.33	4.63	12.37
fac(N)-$[Co(Clacac)(i\text{-dtma})]ClO_4$	$CoC_{11}H_{20}O_8N_3Cl_2$	452.14	28.98	4.52	9.29	29.22	4.46	9.29
fac(N)-$[Co(Iacac)(i\text{-dtma})]ClO_4$	$CoC_{11}H_{20}O_8N_3ClI$	543.59	24.31	3.72	7.74	24.30	3.71	7.73
fac(N)-$[Co(O_2Nacac)(i\text{-dtma})]ClO_4$	$CoC_{11}H_{20}O_{10}N_4Cl$	462.69	28.55	4.54	11.85	28.56	4.36	12.11
mer(N)-$[Co(Clacac)(i\text{-dtma})]ClO_4$	$CoC_{11}H_{20}O_8N_3Cl_2$	452.14	28.99	4.57	9.28	29.22	4.46	9.29
mer(N)-$[Co(Iacac)(i\text{-dtma})]ClO_4$	$CoC_{11}H_{20}O_8N_3ClI$	543.59	24.15	3.71	7.72	24.30	3.71	7.73

(acac)(*i*-dtma)]ClO$_4$ were successful. The single unsuccessful attempt at nitration was due to the insolubility of the complex in the nitration reagent. The results of the elemental analysis of the complexes obtained are shown in Table 1. (The results for the brominated species of *i*-dtma complexes have previously been reported.[6])

Preparation of $(+)_{589}$-$[Co(acac)(en)_2](ClO_4)_2$ *and Its Halogenation.* A diastereoisomer of the bis(ethylenediamine) complex, $(+)_{589}$-$[Co(acac)(en)_2][(+)_{589}\text{-}AsOC_4H_4O_6]_2$, was prepared by the standard method.[9] One gram of the diastereoisomer was suspended in 45 ml of ethanol and 5 ml of aqueous 2 M NaClO$_4$ was added. The mixture was stirred at *ca.* 45 °C until the solid phase changed to white (*ca.* 30 min). After the solid ($(+)_{589}$-$AsOC_4H_4O_6Na$) was removed by filtration, the orange-red filtrate was concentrated to *ca.* 10 ml, whereupon an additional white precipitate resulted, which was then removed. The filtrate was then placed overnight in a refrigerator, and the red crystals thus formed were collected and washed with ethanol and ether. Yield, 0.5 g. $[\alpha]_{589}=+478°$, $[\alpha]_{405}=-2475°$. The specific rotation was not changed by recrystallization.

The halogenation of the optical isomer was carried out in the same manner as that for the inactive complex. $[\alpha]_{589}=+506°$, $[\alpha]_{405}=-2600°$ for the chlorinated complex, $[\alpha]_{589}=+473°$, $[\alpha]_{405}=-2440°$ for the brominated complex, and $[\alpha]_{589}=+460°$, $[\alpha]_{405}=-2395°$ for the iodinated complex.

Results and Discussion

Absorption Spectra. The absorption spectra of $[Co(acac)(en)_2](ClO_4)_2$ and its halogenated and nitrated species, as well as those of $[Co(acac)_3]$ and $[Co(Xacac)_3]$ (X=Cl, Br, I, NO$_2$) are shown in Figs. 1 and 2. The spectra of the other set of complexes with the same ammine or amine ligand have patterns quite similar to those of the set of bis(ethylenediamine) complexes, some of which have been presented elsewhere.[6,7,10] The numerical values of the absorption maxima are summarized in Table 2.

Since the halogenation and nitration of $[Co(acac)_3]$ have been well-established, the spectral variations observed between the spectrum of $[Co(acac)_3]$ and those of $[Co(Xacac)_3]$ may be adopted as an indication of the substitutions at the methine of the ligand. Thus, as may be seen in Fig. 1 and Table 2, the wave numbers

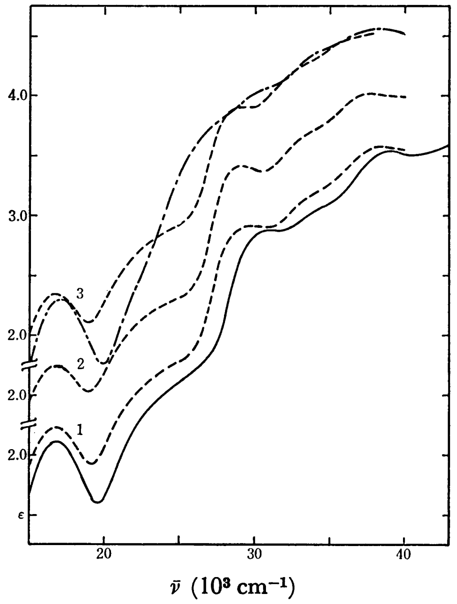

Fig. 1. Absorption spectra of $[Co(acac)_3]$ and its halogenated and nitrated species.

—: $[Co(acac)_3]$ ---1: $[Co(Clacac)_3]$
-·-: $[Co(O_2Nacac)_3]$ ---2: $[Co(Bracac)_3]$
---3: $[Co(Iacac)_3]$

TABLE 2. ABSORPTION MAXIMA OF ACETYLACETONATOCOBALT(III) COMPLEXES AND THEIR HALOGENATED AND NITRATED SPECIES

	I		Sp	
	$\tilde{\nu}(10^3\text{cm}^{-1})$	(ε)	$\tilde{\nu}(10^3\text{cm}^{-1})$	(ε)
$[Co(acac)(NH_3)_4](ClO_4)_2$	19.70	(92.0)	30.91	(4500)
$[Co(Clacac)(NH_3)_4](ClO_4)_2$	19.70	(111.4)	29.41	(4660)
$[Co(Bracac)(NH_3)_4](ClO_4)_2$	19.70	(113.6)	29.41	(4440)
$[Co(Iacac)(NH_3)_4](ClO_4)_2$	19.70	(119.6)	28.94	(3760)
$[Co(O_2Nacac)(NH_3)_4](ClO_4)_2$	20.10	(93.6)	*ca.* 31	(*ca.* 4100)
$[Co(acac)(en)_2](ClO_4)_2$	20.04	(139.4)	30.72	(4200)
$[Co(Clacac)(en)_2](ClO_4)_2$	20.04	(163.2)	29.16	(4200)
$[Co(Bracac)(en)_2](ClO_4)_2$	20.04	(164.8)	29.16	(3960)
$[Co(Iacac)(en)_2](ClO_4)_2$	20.04	(171.2)	28.86	(3560)
$[Co(O_2Nacac)(en)_2](ClO_4)_2$	20.49	(140.6)	*ca.* 31	(*ca.* 3900)
α-$[Co(acac)(trien)](ClO_4)_2$	20.20	(151.8)	30.77	(4240)
α-$[Co(Clacac)(trien)](ClO_4)_2$	20.20	(171.4)	29.24	(4220)
α-$[Co(Bracac)(trien)](ClO_4)_2$	20.20	(173.6)	29.20	(3900)
α-$[Co(Iacac)(trien)](ClO_4)_2$	20.20	(180.4)	28.86	(3480)
α-$[Co(O_2Nacac)(trien)](ClO_4)_2$	20.62	(152.8)	*ca.* 31	(*ca.* 3800)
β-$[Co(acac)(trien)]Br_2$	19.92	(206.6)	30.63	(3800)
β-$[Co(Clacac)(trien)](ClO_4)_2$	19.92	(223.2)	29.11	(3800)
β-$[Co(Bracac)(trien)](ClO_4)_2$	19.92	(233.6)	29.07	(3640)
β-$[Co(Iacac)(trien)](ClO_4)_2$	19.92	(237.6)	28.82	(3320)
β-$[Co(O_2Nacac)(trien)](ClO_4)_2$	20.41	(227.2)	*ca.* 31	(*ca.* 3800)
fac(*N*)-$[Co(acac)(i\text{-}dtma)]ClO_4$	18.98	(170.0)	30.72	(4120)
fac(*N*)-$[Co(Clacac)(i\text{-}dtma)]ClO_4$	19.01	(182.0)	29.24	(4020)
fac(*N*)-$[Co(Bracac)(i\text{-}dtma)]ClO_4$	19.01	(184.8)	29.20	(3800)
fac(*N*)-$[Co(Iacac)(i\text{-}dtma)]ClO_4$	19.05	(188.8)	28.90	(3520)
fac(*N*)-$[Co(O_2Nacac)(i\text{-}dtma)]ClO_4$	19.46	(185.8)	*ca.* 31	(*ca.* 3800)
mer(*N*)-$[Co(acac)(i\text{-}dtma)]ClO_4$	19.84	(157.6)	30.58	(4160)
mer(*N*)-$[Co(Clacac)(i\text{-}dtma)]ClO_4$	19.92	(176.6)	28.94	(4160)
mer(*N*)-$[Co(Bracac)(i\text{-}dtma)]ClO_4$	19.92	(178.6)	28.90	(3980)
mer(*N*)-$[Co(Iacac)(i\text{-}dtma)]ClO_4$	19.92	(184.8)	28.65	(3600)

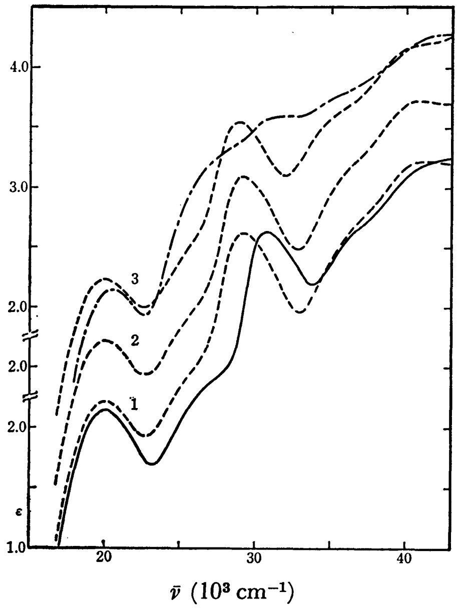

Fig. 2. Absorption spectra of $[Co(acac)(en)_2](ClO_4)_2$ and its halogenated and nitrated species.
—: $[Co(acac)(en)_2](ClO_4)_2$
-·-: $[Co(O_2Nacac)(en)_2](ClO_4)_2$
---1: $[Co(Clacac)(en)_2](ClO_4)_2$
---2: $[Co(Bracac)(en)_2](ClO_4)_2$
---3: $[Co(Iacac)(en)_2](ClO_4)_2$

of the first bands of $[Co(Xacac)_3]$ (X=Cl, Br, I) are nearly equal to that of $[Co(acac)_3]$, whereas the intensities of the formers are rather higher than that of the latter. The specific band arising around 30×10^3 cm^{-1} (which has been attributed to the transition of an electron from the metal t_{2g} to the ligand π^* orbitals[11]) shifts to lower wave numbers with nearly equal intensity upon halogenation. These spectral movements are observable, with a slightly modified and rather pronounced feature, between the spectra of each group containing an acetylacetonato complex and its halogenated species, as may be seen in the figure and the table.

The spectral shift of $[Co(O_2Nacac)_3]$ from $[Co(acac)_3]$ may be summarized as follows. First, the first band shifts to a higher wave number with an increase in the band intensity. Second, the specific band expands with a considerable deformation of the band feature, and no clear maximum is observable. This expansion and deformation probably comes from an overlap of the absorption of the nitro group (*ca.* 27×10^3 cm^{-1}) onto the $\pi^*\leftarrow t_{2g}$ band. These spectral variations are also observable in each spectrum of the nitrated complexes, although the increase in intensity of the first band is very small in a few cases.

Thus, the absorption spectra, together with the results of the elemental analysis and NMR spectra described below, indicate that all the acetylacetonato complexes studied have been substituted by halogens and all but *mer*(*N*)-[Co(acac)(*i*-dtma)]ClO_4 by a nitro group at the methine of the ligand. The spectral relationships for the complexes can be summarized as follows:

(1) with respect to the first bands,

$$\bar{\nu}_{\mathrm{acac}} \simeq \bar{\nu}_{\mathrm{Clacac}} \simeq \bar{\nu}_{\mathrm{Bracac}} \simeq \bar{\nu}_{\mathrm{Iacac}} \text{ and } \bar{\nu}_{\mathrm{acac}} < \bar{\nu}_{\mathrm{O_2Nacac}}$$

$$\varepsilon_{\mathrm{acac}} < \varepsilon_{\mathrm{Clacac}} < \varepsilon_{\mathrm{Bracac}} < \varepsilon_{\mathrm{Iacac}} \text{ and } \varepsilon_{\mathrm{acac}} \leqslant \varepsilon_{\mathrm{O_2Nacac}}$$

(2) with respect to the specific bands,

$$\bar{\nu}_{\mathrm{acac}} > \bar{\nu}_{\mathrm{Clacac}} \simeq \bar{\nu}_{\mathrm{Bracac}} > \bar{\nu}_{\mathrm{Iacac}}$$

$$\varepsilon_{\mathrm{acac}} \simeq \varepsilon_{\mathrm{Clacac}} > \varepsilon_{\mathrm{Bracac}} > \varepsilon_{\mathrm{Iacac}}$$

NMR Spectra. The proton NMR spectra were measured to further verify the substitutions at the methine of the ligand. The resonances of the methine protons observed around 4.5 ppm in the spectra of the unsubstituted complexes disappeared completely in those of the substituted complexes, supporting our identification. As an illustration, a set of representative spectra is shown in Fig. 3.

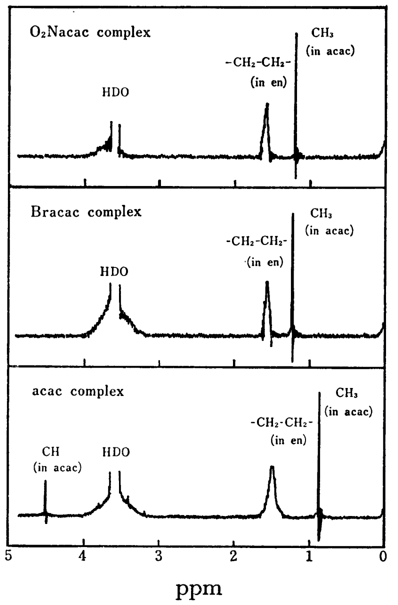

Fig. 3. NMR spectra of [Co(acac)$(en)_2$]$(ClO_4)_2$ and its brominated and nitrated species.

Preparation. Acetylacetonatobis(ethylenediamine)-cobalt(III) is usually obtained as an iodide salt owing to its ease of isolation.[9] Bromination of the iodide salt was also attempted using *N*-bromosuccinimide. However, a redox reaction appeared to occur simultaneously, and the reaction product was too complicated to isolate the brominated species. The perchlorate salt 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, this property is rather suitable for the substitutions, and no trouble was found in this regard. The property was also utilized to convert $(+)_{589}$-[Co(acac)$(en)_2$][$(+)_{589}$-$AsOC_4H_4O_6$]$_2$ into $(+)_{589}$-[Co(acac)$(en)_2$]$(ClO_4)_2$. The lack of success in the bromination of [Co(acac)$(en)_2$]$^{2+}$ by Collman *et al.*,[5] although the detail of their procedure is not available, is assumed to be due simply to an unsuitable counter anion. A more or less similar situation was experienced for the other acetylacetonato complexes, and since *β*-[Co(acac)(trien)]$(ClO_4)_2$ is especially soluble in the organic solvents, the bromide salt, which is a little easier to handle in isolation, was used as the starting substance.

The halogenated and nitrated species, in general, are less soluble in water and have better crystallizability than their parent complex. Thus, in the cases of the halogenations, the substituted complex sometimes appears as crystals during the reaction.

Characteristics of the Substitution Reactions. Because of the very similar behavior of the chelated acetylacetonate ion to that of the aromatic hydrocarbons, it is widely accepted that these substitution reactions are ionic rather than radical processes. It has therefore been argued[4a)] on this assumption that, because of the electrostatic interaction between the substrates and the electrophiles, cationic acetylacetonatometal complexes are more resistant to substitutions at the methine than neutral and anionic complexes. However, our results indicate that this is not necessarily true, since the substituted complexes were obtained easily and without distinct differences in yields by similar procedures for substrates which were unipositive and dipositive. A quantitative comparison of the rate of chlorination also indicated that the charge of the complex was not a dominant factor in the substitution,[10)] and rather the degree of distortion from the regular octahedron structure appeared to be more influential since the dipositive *β*-trien complex was the most reactive. The following is a possible explanation for this minor effect of the net charge of the complex upon the reactions.

According to the Pauling electroneutrality principle, the net charge of a complex ion is distributed among the atoms which exist on the surface of the ion. Thus, the methine hydrogen must be more positive, as the net

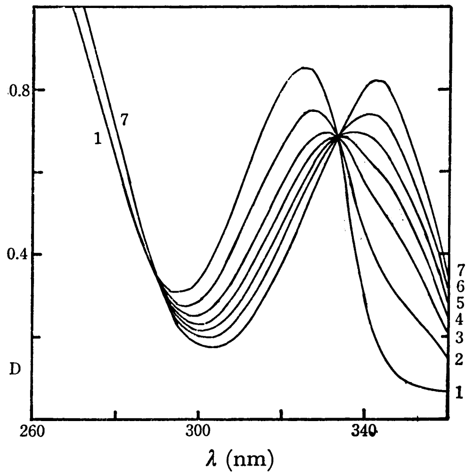

Fig. 4. A change of the absorption curve of [Co(acac)-$(en)_2$]$^{2+}$ in the presence of *N*-chlorosuccinimide. Condition: [Comp]$=2\times10^{-4}$ M, [NCS]$=3\times10^{-4}$ M, [$HClO_4$]$=2\times10^{-3}$ M, Temp=40 °C.
1: 0 min (the reactant complex without NCS), 2: after 10 min, 3: after 25 min, 4: after 40 min, 5: after 60 min, 6: after 100 min, 7: after ∞ min and the resultant complex.

Table 3. Rate constants, k, for the chlorination of $[Co(acac)(en)_2]^{2+}$ by N-chlorosuccinimide

No.	[Complex] $\times 10^{-4}$M	[NCS] $\times 10^{-4}$M	$[HClO_4]$ $\times 10^{-3}$M	[Other Substances]	Temp °C	x_{40} %	k $\times 10^2$ mol^{-1} min^{-1}
1	2	3	2	0	35	57.2	1.01b)
2	2	3	2	0	40	65.3	1.36b)
3	2	3	2	0	45	74.4	1.97c)
4	2	3	4	0	40	66.1	1.41b)
5	2	3	2	$[NaClO_4]=1\times 10^{-2}$M	40	65.9	1.42b)
6	2	3	2	$[C_2H_5OH]=50\%$	40	55.5	0.98b)
7	2	6	2	0	40	90.7	1.35c)
8	2a)	3	2	0	40	65.1	1.36b)
9	2a)	0	2	0	40	no change in rotation and absorption	
10	2a)	3	2	0	40	change in rotation: −0.247° → −0.280° at 405 nm	
11	2	2	2	0	40	48.0	x_∞ (%)=80.8

a) An optical active isomer was used. b) The average value calculated from x_{10}, x_{25}, x_{40}, x_{60}, and x_{100}. c) The average value calculated from x_{10}, x_{25}, x_{40}, and x_{60}.

charge of the complex ion increases. This means that the methine carbon in the more positive ion is possibly the more negative and is the more reactive with the electrophilic reagents. It may be considered that the increase in reactivity compensates the effect of the electrostatic repulsion between the complex cation and the electrophile.

In order to examine the above consideration and to clarify the reaction pathway, some kinetic measurements were carried out on the chlorination of $[Co(acac)(en)_2]^{2+}$. A spectral change is illustrated in Fig. 4 and the concentrations of the complex during the reaction were obtained from the optical densities at 343 nm. The result of the measurements is summarized in Table 3.

In order to obtain the rate constant, it was at first assumed that the reaction was of the second order and obeyed the quation,

$$k = \frac{2.303}{(b-a)}\frac{1}{t}\log\frac{a(b-x)}{b(a-x)}$$

where a and b are the initial concentrations of the reactant complex and N-chlorosuccinimide (NCS), respectively. However, the values of k calculated at different times in a run are not in agreement, but decrease as the time increases. Since the isosbestic points at 290 and 333 nm were strictly maintained during the reaction, it is certain that the only reaction of the reactant complex was the chlorination. Therefore, the cause of the decrease in k with time must reside in a reaction of NCS, which consumes NCS without chlorinating the complex. This assumption was confirmed by an equimolar experiment (No. 11), in which x_∞ was not 100%, but 80.8%. Thus, the kinetic equation can be assumed to be

$$\frac{dx}{dt} = k(a-x)(b-(1+c')x) = k(a-x)(b-cx)$$

and

$$k = \frac{2.303}{(b-ac)}\frac{1}{t}\log\frac{a(b-cx)}{b(a-x)}$$

where c can be estimated from the equimolar experiment as

$$\frac{19.2}{80.8} = \frac{c'}{1} \qquad c = 1 + c' = 1.238$$

With this approximation, the values of k in a run agree to within 3% of each other and the values thus obtained are tabulated in the table.

Several characteristics can be pointed out from the table.

(1) Without NCS, the reactant complex, involving the optical active complex, is stable under the conditions of these experiments. (No. 9).

(2) The rate in the ethanol(50%)-water mixture is considerably smaller than those in aqueous solutions. (No. 6).

(3) An increase in the concentration of $HClO_4$, as well as of $NaClO_4$, hardly accelerates the velocity. (Nos. 4, 5).

(4) The optically active isomer reacts with the same velocity as the inactive complex, as expected. (No. 8).

(5) The optical rotation increases with the evolution of the reaction, and α_∞ is identical with the value calculated from the rotation of the isolated active $[Co(Clacac)(en)_2](ClO_4)_2$. (No. 10).

The kinetic equation and these characteristics of the reaction may, as a whole, indicate that the reaction proceeds with a direct attack of NCS molecule onto the substrate, for which no bond rupture between the metal and the ligands is involved as an activation process. It is also supposed that the dipolar water molecules surrounding the reactants have sufficient power to activate the reactant ions and molecules.

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