powder, which was purified by silica gel column using benzene as an elution solvent to afford 5.8 g of 24-hydroxycholesteryl acetate (6),[14] mp 124—125°, identified by comparison with the authentic sample.

Reaction of 24-Hydroxycholesteryl Acetate (6) with P_2O_5——To a stirred suspension of P_2O_5 (160 mg) in 10 ml of dry benzene, **6** (200 mg) was added dropwise under ice-cooling. After stirring for 20 min at 7,° the reaction mixture was extracted with ether, washed with saturated $NaHCO_3$ solution and then with brine. Evaporation of the solvent afforded a slight yellow amorphous powder (198 mg), which was purified by column chromatography on silica gel. The fraction eluted with benzene–hexane (1: 4) gave 163 mg of desmosteryl acetate (**3**), mp 93—94.5.

The GLC analysis of the crude product using 1.5% OV-1 on Chromosorb WHP, 150 cm × 3 mm i.d. at 270°, demonstrated that 23-dehydrocholesteryl acetate (**10**) (3%) and **6** (4%) were contained in the reaction product. The retention times of **10**, **3** and **6** were 3.2, 3.6 and 6.0 min, respectively. 23-Dehydrocholesteryl acetate was identified in respect to the retention time of GLC and mass spectrum obtained by GC-MS system with an authentic sample.[15]

Reaction of 24-Hydroxycholesteryl Acetate (6) with $POCl_3$——In a solution of **6** (200 mg) in pyridine (5 ml), phosphorus oxychloride (0.5 ml) was added and the mixture was stirred for 3.5 hr at 20°. The solution was poured into ice-water and extracted with ether. The ether solution was washed with 1N HCl and then with brine. Evaporation of the solvent afforded a slight yellow amorphous powder (200 mg) which was purified by column chromatography. The fraction eluted with benzene–hexane (1: 4) gave desmosteryl acetate (109 mg) and the fraction eluted with benzene–hexane (1.5: 4) gave 24-chlorocholesteryl acetate (**9**) (69 mg), Mass Spectrum *m/e*: 404 (M^+-AcOH), 402, 351, 255, 253, 213; NMR δ, 0.68 (3H, s, 18-Me), 1.02 (3H, s, 19-Me), 2.02 (3H, s, Ac), 3.75 (1H, m, 24-H), 4.60 (1H, m, 3-H), 5.37 (1H, m, 6-H).

The GLC analysis of the crude product indicated that a small amount (2%) of 23-dehydrocholesteryl acetate (**10**) was contained in the reaction product. The yield of **3** and **9** in Table II were calculated from the chromatogram. The column conditions were same as above description. The retention time of **9** was 7.0 min.

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Halogenation Reaction of Bis(acetylacetonato)nickel(II) and -cobalt(II) Chelate

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Introduction of chlorine, bromine, and iodine atom into the ring of labile bivalent metal acetylacetonates, bis(acetylacetonato)nickel (II) and -cobalt(II) chelates, is effected by N-halosuccinimide in carbon tetrachloride. Infrared and ultraviolet spectra of halogenated metal(II)-acetylacetonate chelate derivatives were measured. The masses of substituent at the central carbon atom of these metal(II)-acetylacetonates affected the frequencies of C=O and C=C stretching bands.

The introduction of substituents at the central carbon atom of the trivalent metal-acetylacetonate ring, such as cobalt(III), chromium(III), and rhodium(III), *etc.*, by electrophilic

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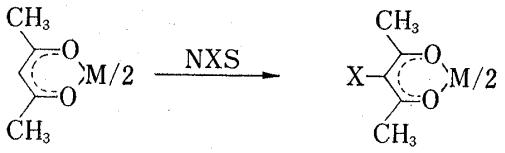

M=Co, Ni X=Cl, Br, I

Chart 1

substitution reactions has been reported by many workers.[2-13] The present paper describes the introduction of a halogen at the central carbon atom of the less stable nickel(II)- and cobalt(II)-acetylacetonate rings in the manner of quasi-aromatic system (Chart 1). N-Halosuccinimides (NXS; X=Cl, Br, and I) are very effective halogenating reagents for these less stable chelates, and carbon tetrachloride and ether are good solvents for the halogenation reactions by NXS.

Bis(acetylacetonato)nickel(II) and -cobalt(II) chelates usually exist as dihydrate and polymeric solid,[14] which are less soluble in carbon tetrachloride. Water is removed from these dihydrate molecules by heating to 100—110° under a reduced pressure. The dehydrated substances are easily soluble in carbon tetrachloride, benzene, and ether.

Treatment of these chelates by NXS in carbon tetrachloride afforded bis(3-haloacetylacetonato)nickel(II) and -cobalt(II) chelates. These halogenated derivatives tend to decompose in water. Carbon tetrachloride is effective for electrophilic halogenation reactions of these water-sensitive complexes. However, bis(3-iodoacetylacetonato)nickel(II) and -cobalt(II) complexes tend to decompose in the solvent.

Infrared Spectra

Infrared (IR) spectra of nickel(II) and cobalt(II) complexes resemble each other quite closely in the 400—650 cm^{-1} region. These spectra are also similar to the IR spectra of tris(acetylacetonato)cobalt(III) and -chromium(III), and bis(acetylacetonato)copper(II) chelates. The main IR bands of bis(acetylacetonato)nickel(II) and -cobalt (II) chelates and these halogenated derivatives are shown in Table I.

Table I. Infrared Bands (KBr disk; cm^{-1})

Compound	$\nu_{C=O}$, $\nu_{C=C}$	δ_{C-H}	δ_{C-H}
$Ni(acac)_2$	1612 (s), 1518 (s)	1198 (m)	764 (m)
$Ni(Cl\text{-}acac)_2$	1593 (s)	—	—
$Ni(Br\text{-}acac)_2$	1585 (s)	—	—
$Ni(I\text{-}acac)_2$	1565 (s)	—	—
$Co(acac)_2$	1608 (s), 1517 (s)	1198 (m)	765 (m)
$Co(Cl\text{-}acac)_2$	1581 (s)	—	—
$Co(Br\text{-}acac)_2$	1575 (s)	—	—
$Co(I\text{-}acac)_2$	1558 (s)	—	—

(s) strong, (m) medium

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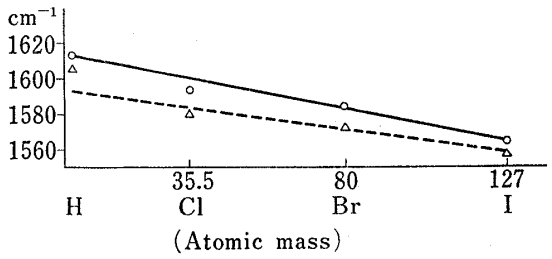

Fig. 1. Correlation between Atomic Mass of Substituent and IR Frequencies of C=O and C=C Stretching Region

○—○: Ni(II) chelates, △—△: Co(II) chelates

TABLE II. Ultraviolet Absorption Data (λ_{max} nm (log ε))

Compound	λ_{max} nm	log ε
$Ni(acac)_2$	296	4.093
$Ni(Cl\text{-}acac)_2$	314	4.113
$Ni(Br\text{-}acac)_2$	316	4.220
$Ni(I\text{-}acac)_2$	324	—
$Co(acac)_2$	292	4.209
$Co(Cl\text{-}acac)_2$	295	4.253
$Co(Br\text{-}acac)_2$	302	4.155
$Co(I\text{-}acac)_2$	—	—

In 1620—1500 cm^{-1} regions, two strong bands have been assigned for mainly C=C and C=O stretching vibration in the chelate ring.[15] The substitution of a halogen atom at the central carbon atom of the chelate ring causes these two bands to become one strong band, which fact may be shown mass effect by the halogen atom.[16] Approximately linear correlation was found between the masses of the halogen atom and frequencies of C=O and C=C stretching vibration in 1620—1500 cm^{-1} region as shown in Fig. 1. Bands at 1198 and 765 cm^{-1} are assigned to C–H bending vibrations. They disappear by halogenation. The IR spectrum is an indicator of the halogenation of metal acetylacetonate.

Ultraviolet Spectra

Ultraviolet (UV) absorption spectra of bis(acetylacetonato)nickel(II) and -cobalt(II) chelates and these halogenated derivatives are recorded in Table II. Iodinated acetylacetone nickel(II) and -cobalt(II) chelates decompose rapidly when irradiated with ultraviolet light.

Expansion of atomic radii of hydrogen atom, and maximum value of halogenated chelates shifted toward longer wavelength due to increased delocalization of the electrons in the ring.

Experimental

All melting points were determined on Yamato Melting Point Apparatus and are uncorrected. IR spectra were measured with a Hitachi EPI-S2 spectrophotometer and UV spectra were measured with a Hitachi EPU-2 spectrophotometer.

Chlorination of Bis(acetylacetonato)nickel(II)——To a solution of $Ni(acac)_2$[17] (100 mg) in CCl_4 (20 ml), N-chlorosuccinimide (104 mg) was added with stirring. The reaction mixture was stirred for 3 hr at room temperature, and then the mixture was allowed to stand for 10 hr at 0°. The precipitate was filtered off, and washed with CCl_4. The filtrate was concentrated to 10 ml under a reduced pressure, and 1 ml of EtOH was added. Pale blue needles crystallized out and was recrystallized from CCl_4 and EtOH. Bis(3-chloro-acetylacetonato)nickel(II), mp 165° (decomp.), was obtained in 42.4% yield. *Anal.* Calcd. for $C_{10}H_{12}O_4Cl_2Ni$: C, 36.81; H, 3.68. Found: C, 36.64; H, 3.96.

Bromination of Bis(acetylacetonato)nickel(II)——To a solution of $Ni(acac)_2$ (100 mg) in CCl_4 (30 ml), N-bromosuccinimide (150 mg) was added with stirring. After stirring for 6 hr at room temperature, the reaction mixture was allowed to stand at 0° for 10 hr. The same treatment as described for the chloride gave bis(3-bromo-acetylacetonato)nickel(II) as blue needles, mp 120° (decomp.) in 19% yield. *Anal.* Calcd. for $C_{10}H_{12}Br_2Ni$: C, 28.92; H, 2.89. Found: C, 28.36; H, 3.23.

Iodination of Bis(acetylacetonato)nickel(II)——To a solution of $Ni(acac)_2$ (100 mg) in CCl_4 (30 ml), N-iodosuccinimide (175 mg) was added with stirring. After stirring for 1 hr at room temperature, the reaction mixture was allowed to stand at 0° for 30 min. Work-up as described for the above chloride gave bis(3-iodo-acetylacectonato)nickel(II) as pale green needles, mp 90° (decomp.) in 28.5% yield. Further purification failed, because the CCl_4 solution tends to decompose slowly.

Chlorination of Bis(acetylacetonato)cobalt(II)——According to the procedure described for nickel(II) chelate, N-chlorosuccinimide (124 mg) was added to a solution of $Co(acac)_2$ (100 mg) in CCl_4 (40 ml) with stir-

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17) $Ni(acac)_2$ indicates the trivial name bis(acetylacetonato)nickel(II) or bis(2,4-pentanedionato)nickel(II) chelate.

ring After stirring for 1 hr at room temperature, the reaction mixture was concentrated to 10 ml under a reduced pressure and was allowed to stand at 0° for 2 hr. The same treatment as described for the chloride of nickel(II) chelate gave bis(3-chloro-acetylacetonato)cobalt(II) as pink needles, mp 134° (decomp.), in 42% yield. *Anal.* Calcd. for $C_{10}H_{12}O_4Cl_2Co$: C, 36.81; H, 3.68. Found: C, 36.64; H, 3.96.

Bromination of Bis(acetylacetonato)cobalt(II)——As described above for nickel(II) chelate, N-bromosuccinimide (139 mg) was added to a solution of $Co(acac)_2$ (100 mg) in CCl_4 (40 ml) with stirring. After stirring for 2.5 hr at room temperature, the reaction mixture was allowed to stand at 0° for 15 hr. The same treatment as described above gave bis(3-bromo-acetylacetonato)cobalt(II) as pink needles, mp 110.5° (decomp.), in 48% yield. *Anal.* Calcd. for $C_{10}H_{12}O_4Br_2Co$: C, 28.92; H, 2.89. Found: C, 29.04; H, 3.15.

Iodination of Bis(acetylacetonato)cobalt(II)——As described above for nickel(II) chelate, N-iodosuccinimide (580 mg) was added to a solution of $Co(acac)_2$ (300 mg) in CCl_4 (50 ml) with stirring. After stirring for 1.5 hr at room temperature, the reaction mixture was allowed to stand at 0°. The same treatment as described above produced bis(3-iodo-acetylacetonato)cobalt(II) as pink needles, mp 102.5° (decomp.), in 35.5% yield. Further purification failed due to decomposition of the iodinated chelate in CCl_4 solution.

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Reaction of Bis(*o*-phenylenediamine)nickel(II) Chloride with Acetylacetone. Synthesis and Properties of Bis(acetylacetonato)(*o*-phenylenediamine)nickel(II) Complex

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The reaction of bis(*o*-phenylenediamine)nickel(II) chloride and acetylacetone is examined and bis(acetylacetonato)(*o*-phenylenediamine)nickel(II) chloride dihydrate and 2,4-dimethyl-1,5-benzodiazepinium chloride were isolated.

The Schiff base of acetylacetone and ethylenediamine, and its metal complexes are well known,[2] but the reaction of *o*-phenylenediamine and acetylacetone in the presence of hydrochloric acid gave the 2,4-dimethyl-1,5-benzodiazepine hydrochloride[3] instead of the 1:2 condensed Schiff base, bis(acetylacetone)-*o*-phenylenediamine.

The present paper describes the synthesis and properties of bis(acetylacetonato)(*o*-phenylenediamine)nickel(II) complex (**3**). A reaction mixture of *o*-phenylenediamine-nickel(II) chloride dihydrate (**1**) and acetylacetone (**2**) in ethanol was stirred at room temperature. Bis(acetylacetonato)(*o*-phenylenediamine)nickel(II) complex (**3**) was obtained as deep red-purple needles, mp 218.5—219°, in 13% yield, together with 2,4-dimethyl-1,5-benzodiazepinium chloride (**4**), mp 131—132°, and its nickel complex as a violet solid.

The infrared spectrum of the complex (**3**) is rather similar to that of the bis(acetylacetonato)(*o*-ethylenediamine)nickel(II) complex, but in the 1600—1500 cm^{-1} region, ethylenediamine Schiff base-nickel(II) complex has two absorption bands of strong intensity at 1590 and 1515 cm^{-1}. While one absorption band of medium intensity at 1559 cm^{-1} and one absorption of strong intensity at 1522 cm^{-1} appear in the case of *o*-phenylenediamine Schiff base-

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