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 hydrochloride³⁾ 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-

1) Location: Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.

2) J. Thiele and G. Steimmig, *Ber.*, **40**, 955 (1907).

3) A. Ouchi, T. Takeuchi, M. Nakatani, and Y. Takahashi, *Bull. Chem. Soc. Japan*, **44**, 434 (1971).

nickel(II) complex, and C-H in-plane bending vibration bands appear at 760 and 772 cm^{-1} , giving sharp medium lines.

The nuclear magnetic resonance spectrum of this diamagnetic complex (3) shows A_2B_2 type resonance lines of phenylene ring at δ 6.65 and 6.95 and methine proton singlet line at δ 5.53 and two methyl proton singlet lines at δ 2.25 and 1.90.

Experimental

Reaction of Bis(o-phenylenediamine)nickel(II) Chloride and Acetylacetone—Bis(o-phenylenediamine)-nickel(II) chloride dihydrate (1.8 g; 0.003 mol) and acetylacetone (1.2 g; 0.012 mol) were allowed to react in EtOH (100 ml) at room temperature with stirring. After stirring for 4 hr, the resulting bis(acetylacetonato)-nickel(II) dihydrate was filtered off, and the violet filtrate was evaporated to dryness and extracted with hot benzene. The wine red extract was evaporated and the residue was recrystallized from benzene-hexane. Bis(acetylacetonato)(o-phenylenediamine)nickel(II) complex (3) was obtained as deep-purple needles, mp 218.5–219° (0.13 g; 13% yield). *Anal.* Calcd. for $C_{16}H_{18}O_2N_2Ni$: C, 58.41; H, 5.48, N, 8.73. Found: C, 58.49; H, 5.53; N, 8.73.

A violet product (1.1 g) was obtained from the insoluble part of the above benzene extraction. It was probably a nickel complex. Treatment of this nickel complex with 10% NaOH gave 2,4-dimethyl-1,5-benzodiazepinium chloride, mp 131–132°. This violet product seems to be a mixture of the nickel complex of 2,4-dimethyl-1,5-benzodiazepinium chloride³⁾ and 2,4-dimethyl-1,5-benzodiazepinium chloride but its purification failed.

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Reaction of Schiff Bases with Trichloroacetyl Chloride in the Presence of Triphenylphosphine

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It has now been found that trichloroacetyl chloride is capable to react with Schiff bases in the presence of triphenylphosphine to give 3,3-dichloro-2-azetidinones. Mechanistically the reaction appears to involve the chlorine cation extraction from the initially formed adduct by triphenylphosphine.

In an earlier paper²⁾ we have reported the 3,3-dichloro-2-azetidinone synthesis by the reaction of Schiff bases of N-benzylideneamine type with trichloroacetic anhydride. It was revealed that this reaction proceeds through the adduct intermediate, N-(α -trichloroacetoxy-

1) Location: 2-2-1, Oshika, Shizuoka.

2) M. Sekiya and T. Morimoto, *Chem. Pharm. Bull.* (Tokyo), 23, 2353 (1975).