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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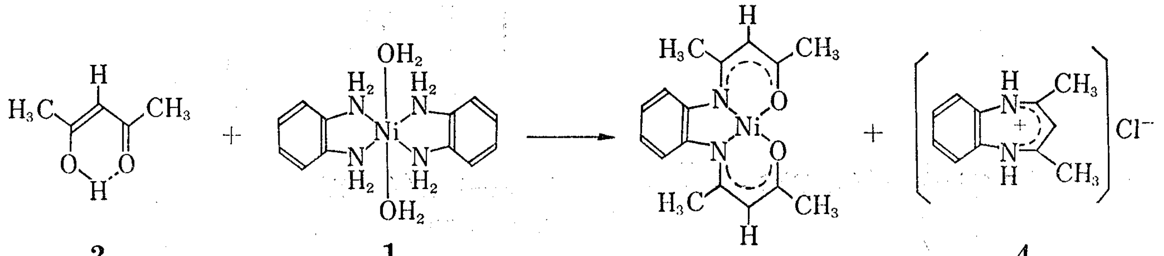
[1] Location: *Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.*

[2] J. Thile 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 sharpmedium 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.



2 1 3 4

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 chloride[3] 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 paper[2] 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-

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[1] Location: *2-2-1, Oshika, Shizuoka.*

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