BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 485—489 (1972)

The Reaction of Bis(acetylacetonato)cobalt(II) with Bromine in Dichloromethane

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(Received July 30, 1971)

When bis(acetylacetonato)cobalt(II) is allowed to react with twice molar quantity of bromine in dichloromethane, cobalt(II) bromide and γ-bromoacetylacetone are produced ultimately. From a deep blue solution of an equimolar reaction mixture at 0°C an intermediary product was isolated and characterized to be dimeric bromo-(acetylacetonato)cobalt(II) by means of elemental analysis and molecular weight determination. The structure of this compound was inferred to be tetrahedral from absorption spectra and magnetic data. Acetylacetonate groups were supposed to act as bridging ligands on the basis of IR data in the lower frequency region. Dibromobis(acetylacetonato)dicobalt(II) was also derived from dibromo(acetylacetone)cobalt(II) by the reaction with sodium acetylacetonate in acetylacetone at 0°C.

It is very interesting that products of reactions between bromine and various metal acetylacetonates in dichloromethane differ depending on the nature of the central metal. Quasiaromatic γ-substitution was observed in cases of beryllium[1] and aluminum[2] acetylacetonates, but copper(II)[3] and cobalt(III)[4] chelates underwent a rupture of chelate rings. In the latter cases copper(II) and cobalt(III) were reduced to lower oxidation states. In the case of the nickel(II) chelate which is known to be trimeric,[5] stepwise displacement of the acetylacetonate ligand by the bromide anion was observed prior to the final breakdown of the trimeric structure, resulting in nickel(II) bromide and γ-bromoacetylacetone.[6]

Bis(acetylacetonato)cobalt(II) is known to exist as a tetrameric molecule in crystals[7] and is trimeric in non-coordinating solvents.[8] Although the oligomeric structure seems to be much less stable in comparison with the trimeric structure of the nickel(II) chelate, some intermediate might be obtained in the reaction with bromine. In order to confirm this view the present study on the reaction between bis(acetylacetonato)cobalt(II) and bromine in dichloromethane has been undertaken, and a dimeric intermediary product dibromobis(acetylacetonato)dicobalt(II) was isolated and characterized.

Results and Discussion

Final Reaction Products. When a dichloromethane solution of bromine was added dropwise to a dichloromethane solution of bis(acetylacetonato)cobalt(II) at room temperature, the original purple color gradually turned violet, blue, and then greenish blue. The solution became turbid when an equimolar bromine was added, and then a yellow green precipitate separated and increased with further addition of bromine. Finally the solution became colorless after twice molar bromine was added to the chelate. The precipitate was filtered, washed, dried *in vacuo* at 130°C, and identified to be cobalt(II) bromide. Found: Co, 26.62; Br, 72.29%. The yield was 0.969 mol/mol of the starting chelate. The organic bromide in the filtrate was determined by iodimetry to be 1.92 g equiv/mol of the starting chelate. Thus the mass balance in the 1 : 2 reaction is given by

$$\mathrm{Co(acac)_2 + 2Br_2 = CoBr_2 + 2acacBr}. \tag{1}$$

Here acac stands for an acetylacetonate anion and acacBr for γ-bromoacetylacetone.

Isolation and Characterization of the Intermediary Product. In order to get some clue to the intermediary product the reaction was studied at 0°C. Even at 0°C when twice molar bromine is allowed to react with bis(acetylacetonato)cobalt(II) in dichloromethane, the same stoichiometry as that at room temperature (1) is observed. On the contrary, when equimolar bromine was added at 0°C, no precipitation took place and the greenish blue solution did not become turbid.

The solution was concentrated by evaporation *in vacuo* at 0°C, to which petroleum ether was added to form a greenish blue precipitate. The precipitate was filtered in a desiccator containing phosphorus pentoxide, washed repeatedly with petroleum ether, and dried *in vacuo* at 100°C. Results of elemental analysis conformed to the formula CoBr(acac). Found: Co, 24.23; Br, 33.32; C, 24.47; H, 3.02%. Calcd for $\mathrm{CoBrC_5H_7O_2}$: Co, 24.77; Br, 33.58; C, 25.24; H, 2.97%. When the 1 : 1 reaction was performed in a mixed solvent of dichloromethane and petroleum ether (1 : 5 in volume) at 0°C, the same compound precipitated without evaporation. This compound is stable in dry state even at room temperature. It is readily soluble in dichloromethane and chloroform, but less soluble in dioxane. When a dichloromethane solution is kept standing at room temperature, decomposition proceeds gradually and the solution becomes turbid after about 10 min. However, a dioxane solution is stable enough to allow determination of molecular weight. Special care was

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[1] Y. Nakamura and S. Kawaguchi, This Bulletin, **40**, 1179 (1967).

[2] Y. Nakamura, M. Hirata, and S. Kawaguchi, *ibid.*, **40**, 2572 (1967).

[3] Y. Nakamura and S. Kawaguchi, *ibid.*, **38**, 954 (1965); T. Ogura, Y. Kojima, Y. Nakamura, and S. Kawaguchi, *ibid.*, **38**, 1468 (1965).

[4] Y. Nakamura, M. Gotani, and S. Kawaguchi, *ibid.*, **45**, 457 (1972).

[5] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965); D. P. Graddon and E. C. Watton, *Nature*, **190**, 906 (1961); F. A. Cotton and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **83**, 2818 (1961).

[6] K. Isobe, Y. Nakamura, and S. Kawaguchi, *Inorg. Nucl. Chem. Lett.*, **7**, 927 (1971).

[7] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965).

[8] J. P. Fackler, Jr., *ibid.*, **2**, 266 (1963); D. P. Graddon, *Nature*, **195**, 891 (1962).

taken in the isolation and manipulation of this compound to exclude atmospheric moisture.

Molecular weight was determined cryoscopically in dioxane to be 445, close to the value 475 calculated for the dimer $[\mathrm{CoBr(acac)}]_2$. However, ebullioscopic determination in a methanol solution gave a value of 252 which is rather near that of monomeric form. It is conceivable that bromo(acetylacetonato)cobalt(II) exists as a dimer in solid state and also in nondonor solvents, but is monomeric in a coordinating solvent such as methanol. Thus the stoichiometry of the 1 : 1 reaction between bis(acetylacetonato)-cobalt(II) and bromine in dichloromethane at 0°C is represented by

$$\mathrm{Co(acac)_2 + Br_2 = \frac{1}{2}[CoBr(acac)]_2 + acacBr.} \tag{2}$$

As shown in Fig. 1 the visible absorption spectrum of this compound in dichloromethane at 0°C is quite different from that of bis(acetylacetonato)cobalt(II) in the same solvent, but resembles that of cobalt(II) bromide in acetone,[9a] which is considered to assume a tetrahedral structure.[9] However, the spectrum in methanol is in turn similar to that of bis(acetylacetonato)cobalt(II) in dichloromethane, where the latter complex is oligomeric and seems to maintain the octahedral structure. These spectral data are well reconciled with the results of molecular weight determination, revealing that bromo(acetylacetonato)-cobalt(II) exists as a tetrahedral dimer in dichloromethane and as an octahedral monomer solvate in methanol.

The effective magnetic moment was determined by the Gouy method to be 4.30 B.M. per g-atom cobalt at room temperature. This value is appreciably lower than 5.02 B.M. at 302.6°K of octahedral bis(acetylacetonato)diaquocobalt(II)[10] and near the usual value of 4.4—4.7 B.M. for tetrahedral cobalt(II) compounds,[9b] supporting again the tetrahedral structure of the dimeric compound in question.

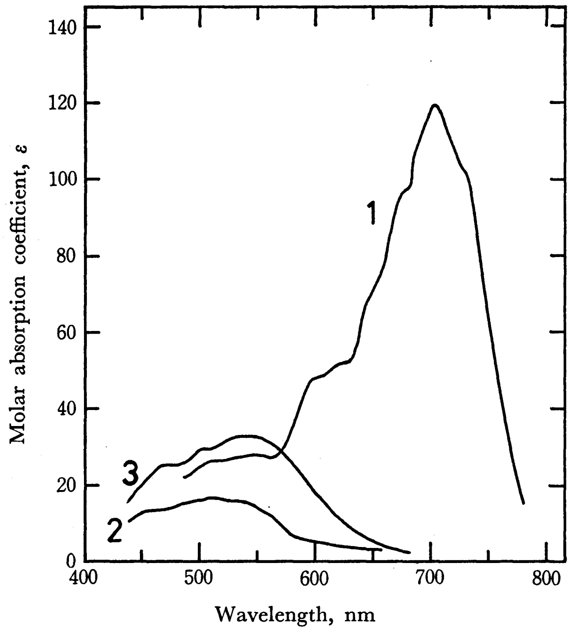

Fig. 1. Absorption spectra of CoBr(acac) in $\mathrm{CH_2Cl_2}$ (curve 1) at 0°C and in methanol (curve 2) at room temperature, and of $\mathrm{Co(acac)_2}$ in $\mathrm{CH_2Cl_2}$ (curve 3).

Bromo(acetylacetonato)cobalt(II) is very hygroscopic and it is difficult to get an IR spectrum showing no band due to water. Broadening of the absorption curve in the 1600—1650 cm^{-1} region (Fig. 2) is due to the OH bending absorption of the contaminant water.

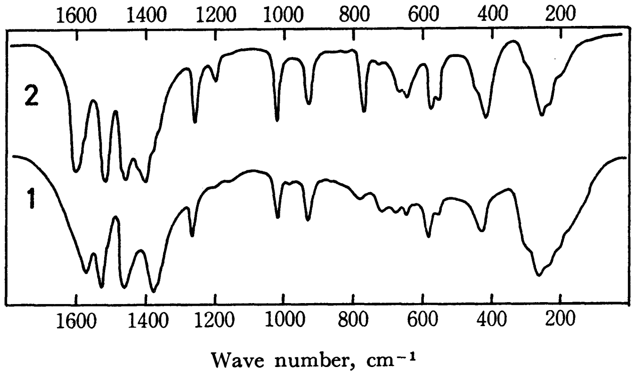

Fig. 2. Infrared spectra of CoBr(acac) (curve 1) and $\mathrm{Co(acac)_2}$ (curve 2) in Nujol.

Absorption bands at 435 and around 260 cm^{-1} are assigned to the Co–O stretching vibration.[11] The former frequency is slightly higher than 422 cm^{-1} observed for bis(acetylacetonato)cobalt(II). Recently Nakamoto and his collaborators[12] studied the Co–Br stretching vibrations of $\mathrm{CoBr_2L_2}$ type complexes (L=py, 4-chloro-py, or 4-bromo-py), and found that the stretching absorption of the bridging Co–Br bond in the polymeric octahedral form appeared at 118—143 cm^{-1}, while that of the terminal Co–Br bond in the monomeric tetrahedral form was observed at 265 cm^{-1}. Brierley, Geary, and Goldstein[13] also assigned 130 and 168 cm^{-1} bands to the stretching vibration of the bridging Co–Br bond in octahedral $\mathrm{CoBr_2}$[1,2-di(4-pyridyl)ethylene], and 247 and 270 cm^{-1} bands to that of the terminal Co–Br bond in tetrahedral $\mathrm{CoBr_2L}$ [L=1-(2-pyridyl)-2-(3-pyridyl)-ethylene, or 1-(2-pyridyl)-2-(4-pyridyl)ethylene]. The present compound shows a quite broad absorption in the 200—320 cm^{-1} region exhibiting a maximum at 270 cm^{-1}. This might be due to the terminal Co-Br stretching, but it is not certain since the parent bis(acetylacetonato)-complex also has a broad maximum at 260 cm^{-1} due to the Co–O stretching vibration. However it could be concluded that no band is observed in the 100—150 cm^{-1} region attributable to the bridging Co–Br stretching, and we propose the structure depicted in Fig. 3 for the dimeric bromo(acetylacetonato)cobalt(II) molecule instead of

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9) a) D. A. Fine, *J. Amer. Chem. Soc.*, **84**, 1139 (1962); b) R. L. Carlin, "Transition Metal Chemistry," Vol. 1, Marcel Dekker, New York (1965), p. 1.

10) F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, **82**, 2979 (1960).

11) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *ibid.*, **83**, 1272 (1961).

12) C. Postmus, J. R. Ferraro, A. Quattrochi, K. Shobatake, and K. Nakamoto, *Inorg. Chem.*, **8**, 1851 (1969).

13) M. Brierley, W. J. Geary, and M. Goldstein, *J. Chem. Soc.* (*A*), **1969**, 2923.

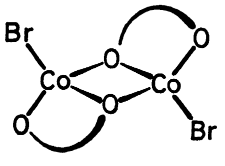

Fig. 3. A proposed structure of dimeric CoBr(acac).

the bromide-bridged structure illustrated previously.[14]

Figure 4 indicates the results of thermogravimetric analysis. The dimeric compound begins to decompose gradually at around 110°C and attains a constant weight at 185°C, but the weight decreases again at around 195°C due to the sublimation of a decomposition product. Heating was discontinued at 300°C and the residue was subjected to elemental analysis. The weight loss by heating up to 185°C was 20.8% corresponding to the release of one acetylacetone group from $[CoBr(acac)]_2$, and acetylacetone collected in a trap cooled by dry ice was identified by gas chromatography.

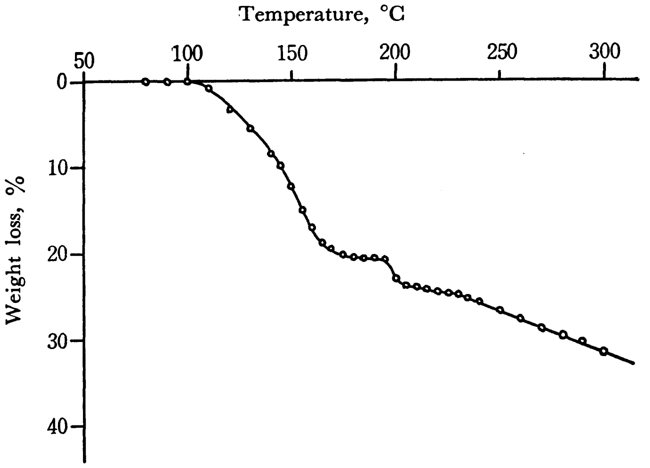

Fig. 4. Thermal decomposition of CoBr(acac) which was dried at 100°C in advance. The rate of temperature elevation was 30°C/hr.

Woodburn and Magee[15] reported that two molecules of dibenzoylmethane (DBMH) were released from an octahedral tetramer, $[Co(DBM)_2]_4$, resulting in a tetrahedral dimer, $(\mathrm{DBM})\mathrm{Co}\genfrac{<}{>}{0pt}{}{\mathrm{OH}}{\mathrm{DBM}}\mathrm{Co}(\mathrm{DBM})$. In the present case a corresponding pyrolytic intermediate could not be identified probably because of the succeeding disproportionation, decomposition, or oxidation as represented by

$$[CoBr(acac)]_2 \rightarrow (CoBr)_2acac \rightarrow Co(acac)_2 + CoBr_2 + \text{Co-oxide(s)}. \quad (3)$$

The sublimate deposited on the glass wall was identified by IR assay to be bis(acetylacetonato)cobalt(II). The decomposition residue (0.1089 g) was found to contain 0.0294 g of cobalt and 0.0505 g of bromine. These values should be compared with 0.0369 g of cobalt and 0.0492 g of bromine in the starting specimen [0.1601 g of CoBr(acac)]. It is apparent that a certain quantity of cobalt was lost as a volatile product, but the whole bromine remained in the residue.

The disproportionation reaction of bromo(acetylacetonato)cobalt(II) was also examined in deaerated dichloromethane. Starting with 0.6121 g (2.57 mmol) of CoBr(acac), 0.1935 g of precipitate resulted after being kept standing at room temperature for 160 hr. This was found to contain 0.0441 g (0.84 mg-atom) of cobalt and 0.1267 g (1.59 mg-atom) of bromine indicating that the precipitate was cobalt(II) bromide contaminated with some impurity. Thus the main reaction is represented by

$$[CoBr(acac)]_2 = CoBr_2 + Co(acac)_2. \quad (4)$$

Dimeric bromo(acetylacetonato)cobalt(II) is rather stable in dichloromethane and the extent of the disproportionation reaction (4) was about 65% even after 160 hr.

Derivation of Dimeric Bromo(acetylacetonato)cobalt(II) from Dibromo(acetylacetone)cobalt(II). A new cobalt(II) complex containing a ketonic molecule of acetylacetone as a ligand was prepared by the reaction between tris(acetylacetonato)cobalt(III) and bromine in dichloromethane and also by direct addition of acetylacetone to anhydrous cobalt(II) bromide.[4] As postulated by Pedersen[16] on the mechanism of the metal-ion catalyzed bromination of β-dicarbonyl compounds, a ketonic molecule of acetylacetone coordinated to cobalt(II) is expected to exhibit enhanced acidity by virtue of the polarization effect of the metal ion. In order to verify the postulate the reaction of the ketonic complex with sodium acetylacetonate as a base was forced to occur in deaerated acetylacetone to yield dimeric bromo(acetylacetonato)cobalt(II) as represented by

$$CoBr_2(acacH) + acacNa \rightarrow \tfrac{1}{2}[CoBr(acac)]_2 + acacH + NaBr. \quad (5)$$

All the procedures of the reaction and separation of products were conducted in a vacuum system to exclude moisture completely. The product obtained after drying at 60°C *in vacuo* was a solvate, $[CoBr(acac)]_2(acacH)$ and was transformed to $[CoBr(acac)]_2$ by prolonged evacuation at 100°C, which showed the same IR and electronic absorption spectra as those of dimeric bromo(acetylacetonato)cobalt(II) obtained by the reaction of bis(acetylacetonato)cobalt(II) with equimolar bromine in dichloromethane at 0°C.

Experimental

Materials. Bis(acetylacetonato)diaquocobalt(II) was prepared by the method of Charles and Pawlikowski[17] and dehydrated to anhydrous bis(acetylacetonato)cobalt(II) by evacuation at 70°C for 7 hr. Found: Co, 22.98;

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[14] Y. Nakamura and S. Kawaguchi, *Chem. Commun.*, **1968**, 716.

[15] S. I. Woodburn and R. J. Magee, *J. Inorg. Nucl. Chem.*, **30**, 2647 (1968).

[16] K. J. Pedersen, *Acta Chem. Scand.*, **2**, 252, 385 (1948).

[17] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

C, 46.28; H, 5.63%. Calcd for Co($C_5H_7O_2$)$_2$: Co, 22.91; C, 46.71; H, 5.49%. Bromine and dichloromethane were purified by the usual methods as described previously.[3] Acetylacetone was distilled under reduced pressure and dried with Molecular Sieves Type 4A8—12, Linde Co.

Reaction of Bis(acetylacetonato)cobalt(II) with Bromine. The reaction of bis(acetylacetonato)cobalt(II) with bromine in dichloromethane was conducted in a three-necked flask equipped with a burette, a glass tube containing phosphorus pentoxide, and another glass tube connected to a filtration equipment by means of polyethylene tubing. To a chelate solution in the flask of the desired concentration, usually in the range 0.05—0.20 M, was added a bromine solution of the same concentration from the burette with vigorous stirring. The precipitate formed was transferred *via* polyethylene tubing to a vacuum filtration apparatus set up in a desiccator containing phosphorus pentoxide. The reaction was performed at 0°C or room temperature, the usual precaution being taken against moisture.

Preparation of Dibromobis(acetylacetonato)dicobalt(II) from Dibromo(acetylacetone)cobalt(II). Dibromo(acetylacetone)cobalt[4] (0.957 g, 3 mmol) was dissolved in about 30 m*l* of acetylacetone in an ampoule (A) connected *via* the ground glass joint to a glass tube containing phosphorus pentoxide. To this solution cooled at 0°C, powder of sodium acetylacetonate (0.366 g, 3 mmol) was added and stirred at 0°C for about 2 hr. Ampoule (A) was then attached to the vacuum line as depicted in Fig. 5, and deaerated by cycles of freezing and thawing. Acetylacetone was then distilled *in vacuo* at 0°C into another ampoule (D) leaving deep blue viscous residue, into which dichloromethane was distilled at 0°C. A deep blue solution resulted containing white powder of sodium bromide. The lower ampoule system was detached from the vacuum line at the ground glass joint (C), and the solution was filtered into ampoule (B) through a glass filter (G). After the solvent was vacuum-distilled back into ampoule (A), ampoule (B) was cut and the deep blue viscous residue was dried *in vacuo* at room temperature and finally at 60°C for 5 hr. Results of elemental analyses of the deep blue powder agreed with the formula [CoBr(acac)]$_2$(acacH). Found: Co, 19.94; Br, 27.16; C, 31.21; H, 4.03%. Calcd for $Co_2Br_2C_{15}H_{22}O_6$: Co, 20.46; Br, 27.74; C, 31.27; H, 3.86%. This adduct lost acetylacetone gradually on evacuation at 100°C and the following analytical results were obtained after 4 hr. Found: Co, 23.14; Br, 31.70; C, 27.54; H, 3.47%. Calcd for $Co_2Br_2C_{10}H_{14}O_4$: Co, 24.77; Br, 33.58; C, 25.24; H, 2.97%. Such poor coincidence suggests the difficulty of complete liberation of excess solvent.

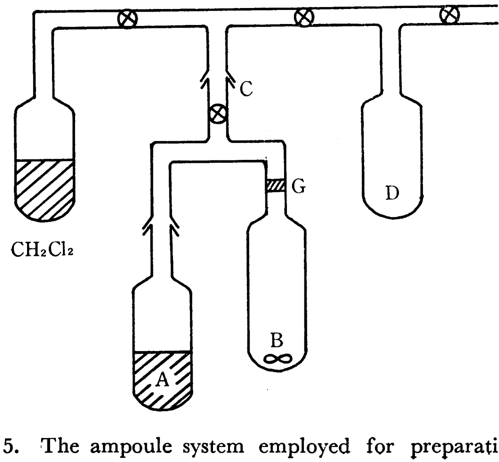

Fig. 5. The ampoule system employed for preparation of CoBr(acac) from CoBr$_2$(acacH).

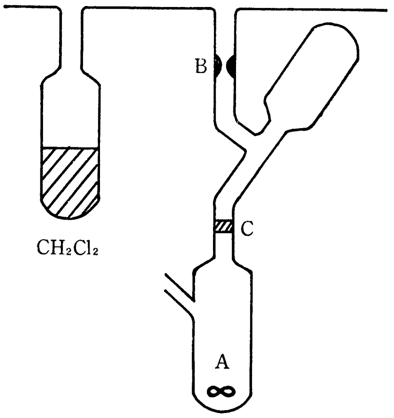

Fig. 6. The ampoule system employed for the disproportionation reaction of CoBr(acac) in dichloromethane.

The Disproportionation Reaction of Dibromobis(acetylacetonato)-dicobalt(II) in Dichloromethane. Dibromobis(acetylacetonato)dicobalt(II) (0.6121 g) was put into an ampoule (A) which had been connected to a vacuum system (Fig. 6), and the side tube was sealed off. In the evacuated ampoule (A) about 40 m*l* of dried dichloromethane was distilled, and the ampoule system was sealed off at B from the vacuum line. The solution was kept at around 25°C with stirring for 160 hr. A green precipitate was separated from the solution by virtue of a glass filter (C), dried and subjected to elemental analysis.

Analyses. Solid products were dried at room temperature *in vacuo* unless otherwise stated. Cobalt was determined gravimetrically as sulfate, and bromine as silver salt. For the determination of organic bromide in the filtrate, the solvent was evaporated under reduced pressure. An acetic acid solution of potassium iodide was added to the residue, and the liberated iodine was titrated with a solution of sodium thiosulfate.

Measurements. Infrared spectra were taken in Nujol on Hitachi EPI-2(4000—700 cm^{-1}), EPI-L(700—200 cm^{-1}), and FIS-3(400—30 cm^{-1}) infrared spectrophotometers. Absorption spectra of solutions were measured by means of a Hitachi EPS-2 recording spectrophotometer. For the observation at 0°C, ice-water was circulated through the cell holder and dry air was forced to blow against the cell window to prevent clouding.

A thermo-spring balance C-282 of Hamada Denki Seisakusho, Ltd. was used for the thermogravimetric analysis, and the heating rate was adjusted to 30°C/hr *in vacuo*. The volatile decomposition product was collected in a trap cooled by dry ice and subjected to gas chromatographic analysis. A column (1.5 m) of Apiezon Grease L on Neosorb NC (Nishio Industries Co., Ltd.) was used at 59°C and hydrogen was passed at a flow rate of 72 cm/min. The decomposition residue was fused with potassium carbonate, and cobalt and bromine contents were determined.

The magnetic susceptibility was measured at room temperature by the Gouy method with an automatic recording magnetic balance (Naruse Kagakukikai Co., Ltd.). The sample was kept together with phosphorus pentoxide in a dry box, and then put quickly into a tube (2 mm in diameter and 70 mm in length) and stoppered with silicone grease.

Molecular weight of bromo(acetylacetonato)cobalt(II) was determined by cryoscopy in dioxane and osmometry in methanol with an apparatus manufactured by Knauer, Germany. Solutions of around 10^{-2} M in the monomer basis were used, and benzil was adopted as a reference.

The authors thank Dr. S. Kawai, Osaka University for the magnetic measurement, and Mr. J. Gohda for the elemental analysis. They are also grateful to the Ministry of Education for financial assistance and to Daicel Co., Ltd. for the supply of acetylacetone.