The Reaction of Tris(acetylacetonato)cobalt(III) with Bromine in Dichloromethane

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(Received June 28, 1971)

Dibromo(acetylacetone)cobalt(II), a new complex containing an acetylacetone molecule as the bidentate ligand, was formed by the reaction of tris(acetylacetonato)cobalt(III) with bromine in dichloromethane, and characterized by elemental and thermogravimetric analyses and electronic and infrared spectra. The same compound was also prepared by direct addition of acetylacetone to anhydrous cobalt(II) bromide. The radical nature of the redox step involved in the reaction pathway from the starting cobalt(III) chelate to the product cobalt(II) complex of acetylacetone was demonstrated by polymerization of methyl methacrylate and styrene remarkably enhanced by the reaction system.

In previous papers we have reported reactions of bromine with several metal acetylacetonates. All metal chelates of this ligand examined so far reacted with bromine quickly in dichloromethane, but products differed depending on the nature of the central metal. In the case of bis(acetylacetonato)copper(II), for instance, the chelate ring was broken, giving γ-bromoacetylacetone and copper(I) bromide or copper(II) bromide according to the reactant mole ratio.[1] In contrast, beryllium and aluminum chelates were so stable as to be subjected to electrophilic ring substitution by bromine at the γ-position of the chelated acetylacetone.[2] Such a direct bromination by elemental bromine without the aid of any buffering mixture was known only for tris(acetylacetonato)-chromium,[3] and the quasiaromatic halogenation[4] of various metal acetylacetonates was effected by making use of *N*-halosuccinimides.[5]

When tris(acetylacetonato)cobalt(III) is allowed to react with excess bromine in dichloromethane, the chelate ring is broken producing cobalt(II) bromide and brominated acetylacetone ultimately. This paper reports the isolation and characterization of a novel cobalt(II) complex of molecular acetylacetone as an intermediary product, and presents some evidence for the radical nature of a redox step involved in the reaction.

Experimental

Materials. Tris(acetylacetonato)cobalt(III) was synthesized according to the standard method.[6] Found: Co, 16.47; C, 50.96; H, 6.22%. Calcd for $Co(C_5H_7O_2)_3$: Co, 16.54; C, 50.57; H, 5.94%. Commercial bromine and dichloromethane were purified by the usual methods.[1] Acetylacetone from Daicel, Ltd. was distilled under reduced pressure and dried with molecular sieves Type 4A8—12, Linde Co. Anhydrous cobalt(II) bromide was prepared by the dehydration of hexahydrate at 135—140°C and purified by sublimation *in vacuo*. Purified methyl methacrylate and styrene were obtained from Prof. Otsu's laboratory and used without further treatment.

Reaction of Tris(acetylacetonato)cobalt(III) with Bromine. The reaction of tris(acetylacetonato)cobalt(III) with bromine in dichloromethane was carried out in a three-necked flask equipped with a burette, a glass tube containing phosphorus pentaoxide, and another tube connected to a filtration equipment by means of a polyethylene tubing. To a chelate solution in the flask of the desired concentration in the range from 0.05 to 0.15 M, was added a bromine solution of the same concentration from the burette with vigorous stirring. The precipitate produced by the reaction was transferred *via* a polyethylene tubing to a vacuum filtration apparatus set up in a desiccator containing phosphorus pentaoxide to remove moisture.

Polymerization Experiments of Vinyl Monomers. When tris(acetylacetonato)cobalt(III) was allowed to react with equimolar bromine in dichloromethane at 0°C, no precipitate was formed. About 10 m*l* of the green solution was quickly transferred to an ampoule, which was then attached to a vacuum line and deaerated by repeated freezing and thawing cycles. Care was taken to keep the sample at temperatures below 0°C. A weighed quantity (about 5 m*l*) of a vinyl monomer was distilled into the ampoule *in vacuo*, which was then sealed off and kept in a thermostat at 35°C for 41 hr. An intermediary compound produced by the reaction between the cobalt(III) chelate and bromine at 0°C underwent further reactions upon heating, concurrently giving rise to the polymerization of a monomer. When the ampoule was opened and the reaction mixture poured into methanol, the cobalt(II) compound was dissolved and a white precipitate of polymer was obtained. This was filtered, washed with methanol and dried *in vacuo*. The polymer specimen for the infrared assay was purified by reprecipitation with benzene-methanol. As a reference the vinyl polymerization was pursued in a similar system including tris(acetylacetonato)cobalt(III) but excluding bromine.

Direct Synthesis of Dibromo(acetylacetone)cobalt(II). About 1 g of anhydrous cobalt(II) bromide was put into an ampoule quickly, evacuated for a while at about 135°C and kept in an ice bath. Into this ampoule about 40 m*l* of purified acetylacetone was distilled *in vacuo*. During the procedure the ice bath was removed occasionally and the reacting mixture was agitated magnetically by means of a small stirrer equipped in the ampoule to prevent aggregation and stimulate dissolution of cobalt(II) bromide. The mixture was then kept at room temperature with continuous stirring. A purple fuzzy product increased as green cobalt(II) bro-

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[1] Y. Nakamura and S. Kawaguchi, This Bulletin, **38**, 955 (1965); T. Ogura, Y. Kojima, Y. Nakamura, and S. Kawaguchi, *ibid.*, **38**, 1469 (1965).

[2] Y. Nakamura and S. Kawaguchi, *ibid.*, **40**, 1179 (1967); Y. Nakamura, M. Hirata, and S. Kawaguchi, *ibid.*, **40**, 2572 (1967).

[3] H. Reihlen, R. Illig, and R. Wittig, *Ber.*, **58B**, 12 (1925).

[4] J. P. Collman, Advan. Chem. Ser., No. 37, p. 78 (1963).

[5] R. W. Kluiber, *J. Amer. Chem. Soc.*, **82**, 4839 (1960); J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *ibid.*, **83**, 531 (1961).

[6] W. C. Fernelius (Ed.), "Inorganic Syntheses," Vol. 5, McGraw-Hill, New York (1957), p. 188.

mide diminished. One or two days were required before the complete disappearance of the latter. The precipitate was increased further by vacuum distillation of some quantity of acetylacetone, filtered and washed with petroleum ether in dry conditions. The product was first evacuated at room temperature. A specimen gave the analytical data: Found: Co, 13,77; Br, 37.84%, which are close to those Calcd for $CoBr_2(C_5H_8O_2)_2$: Co, 14.07; Br, 38.14%. However, the weight decreased gradually with prolonged evacuation. Thus it was finally evacuated at 60°C for about 5 hr to attain constant weight. The color turned from purple to light blue. The compound is very hygroscopic. Found; Co, 18.27; Br, 49.98; C, 19.32; H, 2.83%. Calcd for $CoBr_2(C_5H_8O_2)$: Co, 18.48; Br, 50.12; C, 18.83; H, 2.53%. The purple substance might have contained another molecule of acetylacetone as a solvent of crystallization.

Analysis and Measurements. Solid products were dried *in vacuo* at room temperature and subjected to elemental analysis. Cobalt was determined gravimetrically as sulfate and bromine as silver bromide.

The infrared spectra of solid specimens were measured in Nujol by means of a Hitachi EPI-2 infrared spectrophotometer (4000—700 cm^{-1}) and a Hitachi EPI-L grating infrared spectrophotometer (700—200 cm^{-1}). The infrared spectra of polymers were taken as thin films. Absorption spectra of solutions were obtained using a Hitachi EPS-2 recording spectrophotometer. When the observation was performed at 0°C, ice water was circulated around the cell and dry air was forced to blow against the cell windows to prevent clouding. A solid specimen was ground with Nujol, placed between two plates of opal glass and its transmission spectrum was measured with a Hitachi EPU-2A photoelectric spectrophotometer.[7]

A thermo-spring balance C-282 of Hamada Denki Seisakusho, Ltd. was used for thermogravimetric analysis. The temperature of the sample was raised at a rate of 30°/hr *in vacuo*. The volatile decomposition product was collected in a trap cooled with dry ice and subjected to gas chromatographic analysis. A column of Apiezon Grease L carried on Neosorb NC (Nishio Industries Co., Ltd.) was employed at 59°C, on which hydrogen gas was passed at a flow rate of 72 cm/min. On the other hand the solid decomposition residue was fused together with potassium carbonate. Cobalt and bromine contents were determined gravimetrically.

Magnetic susceptibility was determined at room temperature by the Gouy method with an automatically recording magnetic balance (Naruse Kagakukikai Co., Ltd.). The sample was put into a tube (2 mm in diameter and 70 mm in length) quickly in a dry box. An aqueous solution of nickel(II) chloride was used as a reference.

Results

If tris(acetylacetonato)cobalt(III) is allowed to react with an equimolar quantity of bromine in dichloromethane at 0°C, no precipitate is formed and the dark green solution is quite stable as long as it is kept at 0°C. As shown in Fig. 1 the visible absorption spectrum of this solution is similar to that of the starting complex, suggesting that the intermediary species involved is a cobalt(III) compound. The solution was concentrated by vacuum evaporation at 0°C to isolate a light blue precipitate. The same precipitate was also formed by the addition of petroleum ether. However, the solid thus obtained was no longer soluble in dichloromethane, indicating that this is a different compound from the desired soluble intermediate. Elemental analysis disclosed that the secondary product is a cobalt(II) complex of molecular acetylacetone.[8] Found: Co, 18.96; Br, 50.03; C, 18.24; H, 2.60%.

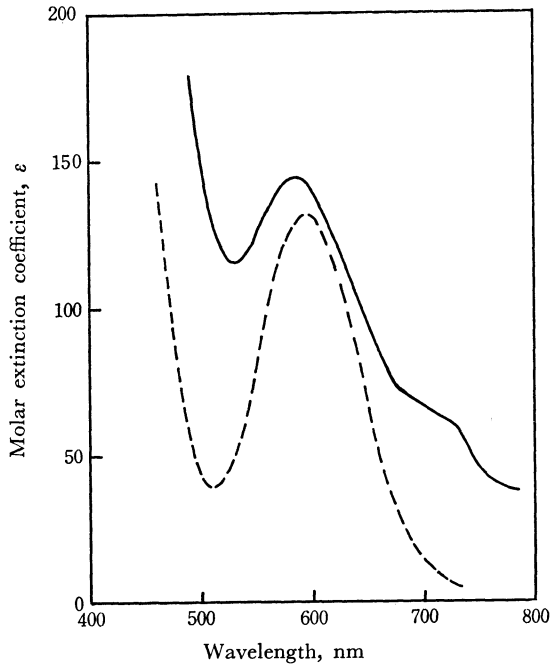

Fig. 1. Absorption spectra in dichloromethane of tris(acetylacetonato)cobalt(III) (----) and a reaction mixture of the chelate and bromine in the mole ratio of 1:1 at 0°C (——).

The infrared spectrum of the new complex $CoBr_2(acacH)$ in Fig. 2 shows a characteristic carbonyl band at 1705 cm^{-1} together with a shoulder at 1720 cm^{-1}, coinciding with those observed at 1707 and 1727 cm^{-1} for ketonic molecules of acetylacetone (Table 1).[9] No absorption bands assignable to enolic molecules or chelated enolate anions are observed. The Co–O stretching absorption at 375 cm^{-1} is lower than 422 cm^{-1} of that in $Co(acac)_2$,[10] reflecting weakness of the Co–O bond in the present complex compared to that in the usual enolate chelate. The spectral data reveal unequivocally that a ketonic molecule of acetylacetone is coordinated to the cobalt atom.

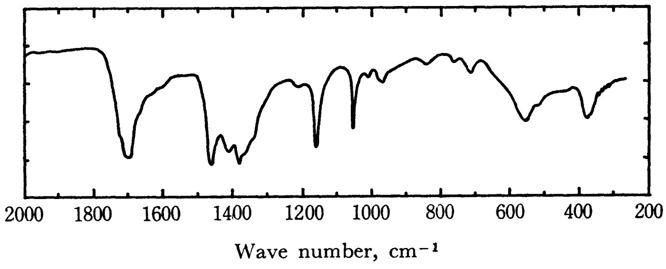

Fig. 2. An infrared spectrum of $CoBr_2(acacH)$ in Nujol mull.

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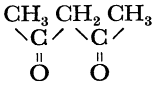
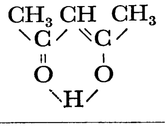
[7] K. Shibata, "Methods of Biochemical Analysis," Vol. 7, ed, by D. Glick, Interscience, New York (1959), p. 77,

[8] A preliminary account of this compound appeared in Y. Nakamura and S. Kawaguchi, *Chem. Commun.*, **1968**, 716.

[9] R, Mecke and E. Funck, *Z. Elektrochem.*, **60**, 1124 (1956).

Table 1. IR data in the carbonyl stretching region (cm^{-1})

$CoBr_2(acacH)$	$Co(acac)_2$	 $CH_3COCH_2COCH_3$	 $CH_3C(O)CHC(O)CH_3$, H
1720 (sh)	—	1727[a]	—
1705	—	1707	—
—	1601	—	1619[a]

a) From ref. 9

The magnetic measurement gave a value of 4.25 B.M. as the effective magnetic moment, indicating the tetrahedral structure[11a] of this cobalt(II) compound.

Since the compound is not soluble in the usual non-coordinating solvents, the absorption spectrum was observed in acetylacetone. The transmission spectrum of a solid specimen was also measured by the Nujol mull method and confirmed to be similar to that in an acetylacetone solution. As depicted in Fig. 3 the absorption curve resembles that observed for $CoBr_2(acetone)_2$ which is considered to assume a tetrahedral structure.[11)]

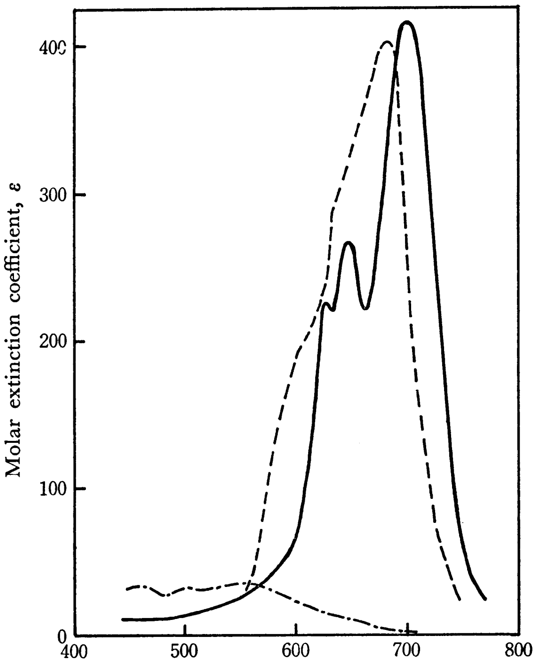


Fig. 3. Absorption spectra of $CoBr_2(acacH)$ in acetylacetone (——), $CoBr_2$ in acetone (----), and $Co(acac)_2$ in dichloromethane (—•—).

In accordance with the supposition that the linkage of acetylacetone to cobalt is weak, the compound begins to decompose at around 70°C. This should be compared with the behavior of bis(acetylacetonato)-cobalt(II), which is quite stable and easily sublimes *in vacuo*. As illustrated in Fig. 4 the weight decrease amounts to 30% which coincides with the value 31% calculated for the loss of acetylacetone. The evaporated substance was collected in a trap cooled with dry ice and identified to be acetylacetone by gas chromatography, while the decomposition residue was characterized to be cobalt(II) bromide by elemental analysis (Found: Co, 27.43; Br, 70.54%).

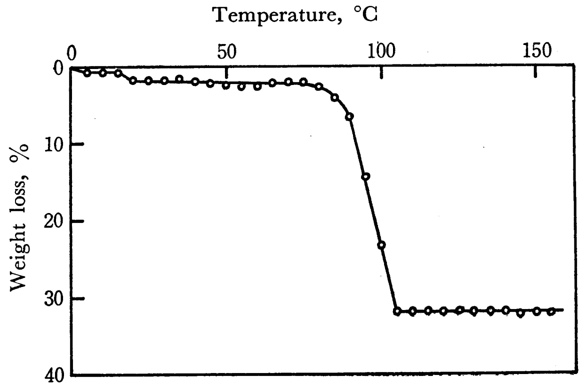


Fig. 4. Thermogravimetric analysis of $CoBr_2(acacH)$. Heating rate: 30°C/hr.

The new complex $CoBr_2(acacH)$ was also prepared by the direct addition reaction of acetylacetone to anhydrous cobalt(II) bromide (see Experimental). Data of the elemental analysis and infrared spectra showed a good coincidence.

When more than 1 mol of bromine was added to 1 mol of tris(acetylacetonato)cobalt(III) in dichloromethane at 0°C, a light blue precipitate appeared. The precipitate produced by the reaction in the reactant mole ratio of 2 : 1 showed an infrared spectrum closely resembling that of $CoBr_2(acacH)$, but gave analytical data showing contamination with cobalt(II) bromide and water. Found: Co, 19.06; Br, 50.64; C, 15.88; H, 2.65; H_2O (Karl Fischer method), 2.82%. Calcd for a mixture $[CoBr_2(acacH)+0.22CoBr_2+0.59H_2O]$: Co, 19.04; Br, 51.63; C, 15.90; H, 2.45; H_2O, 2.82%. Part of the bromine molecules seem to have attacked $CoBr_2(acacH)$, brominating coordinated acetylacetone and liberating cobalt(II) bromide, although the reaction between bromine and a soluble cobalt(III) intermediate occurred predominantly. When a dichloromethane solution of bromine was added dropwise to a dichloromethane solution of tris(acetylacetonato)cobalt(III) at room temperature, a light blue precipitate appeared from the beginning, the amount of which increased with bromine addition. The precipitate was also a mixture of $CoBr_2(acacH)$ and $CoBr_2$. The reaction pattern at room temperature does not differ essentially from that at 0°C, but the reactivity of the cobalt(III) intermediate observed at 0°C (Fig. 1) is much increased at higher temperatures.

A redox process is involved in the conversion of the soluble cobalt(III) intermediate into $CoBr_2(acacH)$. To ascertain the possible radical nature of this redox process, polymerization reactions of methyl methacrylate and styrene were examined in the system. Tris(acetylacetonato)cobalt(III) is known to initiate

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10) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 1272 (1961).

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

TABLE 2. RESULTS OF POLYMERIZATION OF METHYL METHACRYLATE AND STYRENE INITIATED BY $Co(acac)_3$ AND THE $Co(acac)_3$-Br_2 SYSTEM (35°C, 41 hr IN DICHLOROMETHANE)

Monomer	$[Co(acac)_3]$, M	Polymer yield, %	
		$Co(acac)_3$ only	$Co(acac)_3$ + Br_2
MMA	3.41×10^{-2}	2.22	27.6
Styrene	4.11×10^{-2}	0.28	7.7

the radical polymerization of the vinyl monomers,[12,13] but the efficiency is rather low under the present reaction conditions, as shown in Table 2. In contrast the $Co(acac)_3$–Br_2 system exhibits a remarkable initiating ability for vinyl polymerization, revealing that some initiating radicals are formed when the cobalt(III) intermediate is warmed.

The difference in the polymer yield (Table 2) observed for the two monomers reflects the difference in the nature of the monomer. Methyl methacrylate is known to be much more reactive than styrene towards free radicals. The infrared spectrum of a polystyrene film showed a weak but definite absorption peak of the carbonyl group at around 1700 cm^{-1}. This is considered to be due to the acetylacetone radical or its fragment attached to the polymer end. A similar observation was also reported by Otsu, Minamii, and Nishikawa[13] on polystyrene which was prepared employing tris(acetylacetonato)manganese(III) as an initiator. The infrared spectrum of poly(methylmethacrylate) obtained closely resembles those of polymers prepared by virtue of typical radical initiators such as benzoyl peroxide and azobisisobutyronitrile, but the carbonyl bands due to the acetylacetone group can not be discriminated because of a strong absorption by the ester group.

Discussion

Although the starting material was a cobalt(III) complex, the isolated stable products were cobalt(II) compounds. The reaction step in which cobalt(III) was reduced is not clear enough, but the solution resulting from the addition of equimolar bromine to tris(acetylacetonato)cobalt(III) in dichloromethane at 0°C gave an absorption curve similar to that of the original chelate as shown in Fig. 1, indicating that the first soluble intermediate is an octahedral cobalt(III) complex. Attempts to isolate this compound as a pure solid were unsuccessful, but it could be supposed that a binuclear cobalt(III) complex (A) was formed by the reaction represented by Eq. (1). Either bromine atoms or acetylacetone groups are able to function as bridging ligands.

$$Co(acac)_3 + Br_2 \rightarrow 1/2\ \underset{(A)}{[CoBr(acac)_2]_2} + acacBr \qquad (1)$$

TABLE 3. VISIBLE ABSORPTION MAXIMUM OF THE REACTION MIXTURE OF TRIS(ACETYLACETONATO)COBALT(III) AND BROMINE (1:1) TOGETHER WITH THOSE OF RELATED COMPLEXES[a)]

	λ_{max}	$\log \varepsilon$
Reaction mixture in CH_2Cl_2 at 0°C	585	2.16
cis-$[Co(acac)_2(NH_3)_2]Cl$ in H_2O	546	2.12
$[Co(acac)_2en]ClO_4$ in H_2O	538	2.20
cis-$[Co(acac)_2py_2]ClO_4$ in CH_3OH	534	1.94
$[Co(acac)_2bipy]ClO_4$ in CH_3OH	553	2.19

a) R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

Visible absorption bands of several related compounds are shown in Table 3. The absorption maximum of the present solution lies on the longer wavelength side corresponding to the weak field of bromine in comparison with other ligands in Table 3. The value of molar absorptivity, however, is similar to values of the related compounds.

The binuclear intermediate (A) changed to the cobalt(II) compound, $CoBr_2(acacH)$ by addition of petroleum ether, concentration at 0°C, or warming to room temperature. We imagine that disproportionation of the intermediate (A) as expressed by Eq. (2) occurred spontaneously, followed by the redox process (3).

$$[CoBr(acac)_2]_2 \rightarrow \underset{(B)}{[CoBr_2(acac)]} + Co(acac)_3 \qquad (2)$$

$$[CoBr_2(acac)] + RH \rightarrow CoBr_2(acacH) + R\cdot \qquad (3)$$

Here the intermediate (B) is an imaginary compound. Either a solvent molecule or γ-bromoacetylacetone might play the role of the hydrogen donor RH. Similarly the reaction of the intermediate (A) with bromine to produce the ketonic complex will be represented by the following equation followed by (3).

$$1/2\ [CoBr(acac)_2]_2 + Br_2 \rightarrow [CoBr_2(acac)] + acacBr \qquad (4)$$

In one experiment 7.14 mmol of tris(acetylacetonato)cobalt(III) was allowed to react with an equimolar quantity of bromine in dichloromethane at room temperature. After 20 hr 2.97 mmol of $CoBr_2(acacH)$ was isolated. If the overall reaction be reproduced by Eqs. (1), (2) and (3) 2.97 mmol of $Co(acac)_3$ and $7.14-2\times2.97=1.2$ mmol (in the monomer basis) of the dimeric intermediate (A) must be contained in the filtrate. The absorption curve of the solution was calculated on this basis by making use of the spectral data as presented in Fig. 1, and found to nearly coincide with the observed one. This supports the proposed scheme (1) through (3).

If a vinyl monomer is mixed with the intermediate (A) in dichloromethane and warmed to higher temperatures, a monomer molecule (M) may take an acetylacetone radical away from (B) liberating cobalt(II) bromide.

$$CoBr_2(acac) + M \rightarrow CoBr_2 + (CH_3CO)_2CHM\cdot \qquad (5)$$

Alternatively the intermediate (B) might abstract a hydrogen atom predominantly from γ-bromoacetylacetone, the radical produced initiating polymeri-

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[12] E. G. Kastning, H. Naarmann, H. Reis, and C. Berding, *Angew. Chem.*, **77**, 313 (1965).

[13] T. Otsu, N. Minamii, and Y. Nishikawa, *J. Macromol. Sci.-Chem.*, **A2**, 905 (1968).

zation in turn.

Molecular adducts of acetylacetone with antimony(V) and titanium(IV) chlorides were prepared by Rosenheim, *et al.*[14] in 1903, but the bonding nature was not confirmed. The mercury(II) chloride complex $HgCl_2(acacH)$ was studied by Paoloni[15] in detail, and it was concluded on the basis of the carbonyl stretching band at 1698 cm^{-1} that a ketonic molecule of acetylacetone was coordinated to the mercury atom with two carbonyl oxygen atoms. The present complex $CoBr_2(acacH)$ as well as similar nickel(II) complexes reported by van Leeuwen,[16] $[Ni(acacH)_3](ClO_4)_2$, $[Ni(acacH)_2(AcOH)_2](ClO_4)_2$, and $[Ni(acacH)_2(H_2O)_2](ClO_4)_2$, also contain ketonic molecules of acetylacetone.

In contrast, the acetylacetone adduct of dioxobis(acetylacetonato)uranium(VI) was concluded to involve an enolic molecule of acetylacetone as a unidentate ligand on the basis of IR and NMR data.[17] More recently the same bonding nature was established by X-ray analysis of dibromobis(acetylacetone)manganese(II).[18] It is very interesting that two tautomeric forms of acetylacetone can exist in metal complexes, but factors for preference of one form over the other are not clear. More examples are wanted.

The authors thank Dr. S. Kawai of Osaka University for the magnetic measurement, and Mr. J. Gohda for the elemental analyses. They are also grateful to Professor T. Otsu and Dr. S. Aoki for the supply of purified vinyl monomers, and to Daicel Co., Ltd. for the gift of acetylacetone. Aknowledgement is made to the Ministry of Education for financial support.

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[14] A. Rosenheim, W. Loewenstamm, and L. Singer, *Ber.*, **36**, 1833 (1903).

[15] L. Paoloni, *Gazz. Chim. Ital.*, **89**, 2171 (1959).

[16] P. W. N. M. van Leeuwen, *Rec. Trav. Chim. Pay-Bas*, **87**, 396 (1968).

[17] J. M. Haigh and D. A. Thornton, *Inorg. Nucl. Chem. Letters*, **6**, 231 (1970).

[18] S. Koda, S. Ooi, H. Kuroya, Y. Nakamura, and S. Kawaguchi, *Chem. Commun.*, **1971**, 280.