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An NMR Study of Metal Complexes Containing Acetylacetone and Related Compounds. I. The Preparation, Halogenation and NMR Spectra of Cobalt(III) Complexes Containing Acetylacetone and Bis(acetylacetone)ethylenediimine

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A mixed cobalt(III) complex containing both bis(acetylacetone)ethylenediimine and acetylacetone anions, [Co(bean)(acac)] (bean=dianion of bis(acetylacetone)ethylenediimine, acac= anion of acetylacetone), was newly prepared and its electrophilic substitution reaction at the chelate ring protone was studied by means of NCS, NBS, and NIS (NCS, NBS and NIS are the abbreviated forms of *N*-chloro-, *N*-bromo- and *N*-iodosuccinimide). The structures of this complex, [Co(baen)(acac)], and of the halogenated complex were both determined to be of the β-form (*cis* with respect to the coordinated two oxygen atoms of baen) on the basis of their NMR spectra. The ring protons of the imine chelates were found to be more reactive than that of the acetylacetone chelate in the chlorination reaction. Then, a bi-substituted complex, [Co(baen-Cl_2)(acac)], in which two chlorine atomes were attached to the two imine chelate rings, was prepared. Tri-substituted complexes, [Co(baen-X_2)(acac-X)] (X=Cl, Br and I), were also prepared. The quasiaromaticity of both the acetylacetone and imine rings was considered on the basis of their NMR spectra. A new complex, [Co(baen)(OH)(H_2O)], was also prepared in order to assign the NMR spectrum of the complex, [Co(baen)(acac)]. The IR, UV, and visible absorption spectra were also considered.

The quasiaromaticity of the metal-acetylacetonate is quite interesting and has been discussed by several authors. On the basis of their reactivity for the electrophilic substitution reaction, characteristic of aromatic compounds, Collman pointed out that metal-acetylacetonates had an aromatic character.[1,2] He also pointed out that imine complexes of β-diketone underwent electrophilic substitution reactions at the chelate-ring protons, as did acetylacetone complexes.[3] For the imine chelate, however, not such a large benzenoid resonance is expected as for the acetylacetone chelate because of the asymmetric property of the imine chelate.[4] Therefore, the quasiaromaticity of the imine chelate is quite an interesting question.

Under these circumstances, it seemed that it would be worthwhile to study the reactivity of the imine chelate ring towards the electrophilic substitution reaction and to compare the reactivity of the imine chelate ring with that of the acetylacetone chelate ring. Mixed cobalt(III) complex containing both the bis(acetylacetone)ethylenediimine anion (baen) and the acetylacetone anion (acac) was prepared and the halogenation reaction on the chelate ring was examined.

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1) J. P. Collman, *Advan. Chem. Ser.*, No. 37, 78 (1963).

2) J. P. Collman, *Angew. Chem.*, **77**, 154 (1965).

3) J. P. Collman and E. T. Kittelman, *Inorg. Chem.*, **1**, 499 (1962).

4) P. J. McCarthy and A. E. Martell, *ibid.*, **6**, 781 (1967).

Experimental

Preparation of the Complexes. *1) Bis(acetylacetone)ethylenediiminatohydroxoaquocobalt(III),* [Co(baen)-(OH)(H_2O)] (I). Bis(acetylacetone)ethylenediiminatodiaquocobalt(II)[5] (12.5 g, 0.04 mol) was dissolved in 200 m*l* of methanol, 4.0 g of potassium hydroxide in 20 m*l* of water was then added, and the resulting solution was oxidized by sucking air through the solution for 4 to 5 hr. When the solution was allowed to stand overnight, reddish crystals were separated out in a low yield. They were subsequently recrystallized from methanol. Found: C, 45.69; H, 6.34; N, 8.65%. Calcd for $C_{12}H_{21}CoN_2O_4$: C, 45.58; H, 6.70; N, 8.86%.

When the filtrate of the complex I was further concentrated by allowing it to stand for 2 or 3 days in an atmosphere, dark green crystals were separated out. They were subsequently recrystallized from methanol. This dark green complex was assigned to the complex II on the basis of its NMR spectrum.

2) Bis(acetylacetone)ethylenediiminatoacetylacetonatocobalt(III), [Co(baen)(acac)] (II). Bis(acetylacetone)ethylenediiminatodiaquocobalt(II) (25 g, 0.079 mol) was dissolved in 200 m*l* of methanol. Acetylacetone (7.8 g, 0.078 mol) neutralized with potassium hydroxide (10 g) in 100 m*l* of water was then added. The resulting solution was oxidized by sucking air through the solution for 4 to 5 hr. After oxidation was completed, the solution was concentrated under a reduced pressure to a volume of about 200 m*l*. During the course of the concentration, a small amount of bisacetylacetonatocobalt(II) was isolated and filtered off. When the solution was allowed to stand for two days, dark green crystals were separated out. They were subsequently recrystallized from methanol. The yield was about 55%. Found: C, 53.68; H, 6.80; N, 7.36%. Calcd for $C_{17}H_{25}CoN_2O_4$: C, 53.55; H, 6.63; N, 7.35%.

Halogenation of the Complex II. *1) Bis(3-chloroacetylacetone)ethylenediiminatoacetylacetonatocobalt(III),* [Co(baen-Cl_2)(acac)] (III). The methanol solution (40 m*l*) of NCS (2.0 g, 0.015 mol) was added slowly to the methanol solution (40 m*l*) of the complex II (3.8 g, 0.01 mol) at 40°C. After five minutes' stirring, about 100 m*l* of water was added. When the resulting solution was allowed to stand for a day at room temperature, light green crystals were separated out. They were subsequently recrystallized from methanol-water. Yield, about 1.2 g (27%). Found: C, 45.55; H, 5.25; N, 6.25%. Calcd for $C_{17}H_{23}CoCl_2N_2O_4$: C, 45.45; H, 5.16; N, 6.24%.

2) Bis(3-chloroacetylacetone)ethylenediiminato-3-chloroacetylacetonatocobalt(III), [Co (baen-Cl_2) (acac-Cl)] (IV). Method 1. A methanol solution (40 m*l*) of NCS (4.0 g, 0.03 mol) was slowly added to a methanol solution (40 m*l*) of the complex II (3.8 g, 0.01 mol) at about 50°C. The solution was stirred for five minutes and then treated with about 100 m*l* of water, and allowed to stand for a day at room temperature. This gave light green crystals and they were then washed with methanol. Yield, about 3.8 g (79%). Found: C, 42.65; H, 4.54; N, 5.44%. Calcd for $C_{17}H_{22}CoCl_3N_2O_4$: C, 42.22; H, 4.58; N, 5.79%.

Method 2. To a methanol solution (20 m*l*) of the complex III (0.54 g, 0.0012 mol), a methanol solution (10 m*l*) of NCS (0.2 g, 0.0015 mol) was added at 50°C. After five minutes, 50 m*l* of water were added and the solution was allowed to stand for a day. This gave light green crystals, which were subsequently washed with methanol. Yield, about 0.4 g (70%). Found: C, 42.36; H, 4.38; N, 5.52%. Calcd for $C_{17}H_{22}CoCl_3N_2O_4$: C, 42.22; H, 4.58; N, 5.79%.

3) Bis(3-chloroacetylacetone)ethylenediiminato-3-bromoacetylacetonatocobalt(III), [Co(baen-Cl_2)(acac-Br)] (V). To a methanol solution (20 m*l*) of the complex III (0.54 g, 0.0012 mol), a methanol solution (10 m*l*) of NBS (0.3 g, 0.0017 mol) was added at 50°C. After five minutes' stirring, about 50 m*l* of water was added to it. The resulting solution was allowed to stand for a day to give light green crystals, which were subsequently washed with methanol. Yield, about 0.4 g (63%). Found: C, 38.55; H, 4.36; N, 5.29%. Calcd for $C_{17}H_{22}CoBrCl_2N_2O_4$: C, 38.66; H, 4.20; N, 5.30%.

4) Bis(3-bromoacetylacetone)ethylenediiminatoacetylacetonatocobalt(III), [Co(baen-Br_2)(acac)] (VI). This compound was prepared from the complex II and NBS in methanol by the same method as in the case of the dichlorination described in *1)*. Yield, about 4.0 g (71%). Found: C, 36.88; H, 4.24; N, 5.07%. Calcd for $C_{17}H_{23}CoBr_2N_2O_4$: C, 37.94; H, 4.31; N, 5.21%.

5) Bis(3-bromoacetylacetone)ethylenediiminato-3-bromoacetylacetonatocobalt(III), [Co(baen-Br_2)(acac-Br)] (VII). This compound was prepared from the complex II (or the complex VI) and NBS in methanol in the way as described above *2)*. Yield, about 4.5 g (74%) for the method 1 and about 0.5 g (82%) for the method 2. Found for the method 1: C, 33.94; H, 3.55; N, 4.73%. Found for the method 2: C, 33.88; H, 3.47; N, 4.69%. Calcd for $C_{17}H_{22}CoBr_3N_2O_4$: C, 33.64; H, 3.65; N, 4.61%.

6) Bis(3-iodoacetylacetone)ethylenediiminato-3-iodoacetylacetonatocobalt(III), [Co(baen-I_2)(acac-I)] (VIII). This compound was prepared from the complex II and NIS in methanol by the method used in the case of trichlorination. Yield, about 5.0 g (65%). Found: C, 27.21; H, 3.05; N, 3.58%. Calcd for $C_{17}H_{22}CoI_3N_2O_4$: C, 26.94; H, 2.93; N, 3.70%.

Measurements. All the NMR spectra were recorded with a Hitachi R-20 spectrometer (60 MHz) at 35°C. The spectra were measured with about a 5—10% solution of deuterochloroform and/or carbontetrachloride. As the internal reference, chloroform (2.74 τ) (when deuterochloroform was used as the solvent) and tetramethylsilane (when carbontetrachloride was used as the solvent) were used. The infrared absorption spectra were taken on potassium bromide disks with a Hitachi EPI-S2 spectrophotometer. All the visible and ultraviolet absorption spectra were recorded by a Hitachi EPS-3 spectrophotometer, with methanol as the solvent.

Results and Discussion

Synthesis and Halogenation Reaction. The complex II was successfully prepared in a yield of about 55% by oxidizing an alkaline methanol solution containing both bis(acetylacetone)ethylenediiminatodiaquocobalt(II), [Co(baen)(H_2O)$_2$], and acetylacetone. Although the yield was low, it could also be prepared by oxidizing an alkaline

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[5] G. T. Morgan and J. D. Smith, *J. Chem. Soc.*, **127**, 2030 (1925).

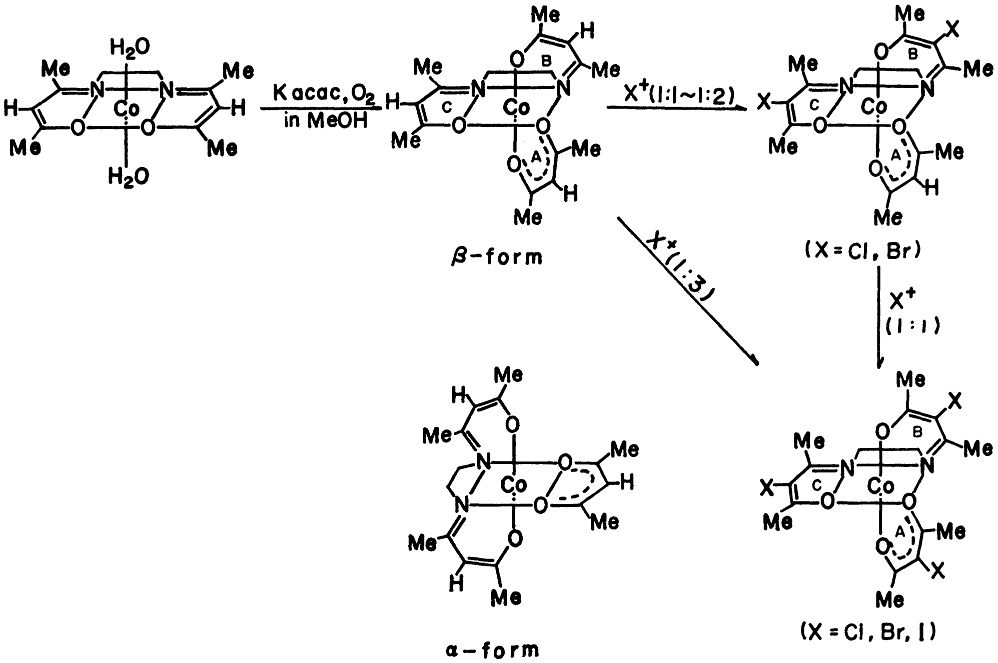


Fig. 1. The preparative scheme and the two geometrical isomers of the complex, [Co(baen)(acac)].

methanol solution containing only the complex, [Co(baen)(H_2O)$_2$]. With both procedures, only the *β*-form complex was isolated. Therefore, it may be presumed that the *β*-form may be preferred in this reaction, for the starting material, [Co(baen)(H_2O)$_2$], takes a planer structure with respect to the two nitrogen atoms and the two oxygen atoms of the coordinated baen. Then, for the two oxygen atoms of baen to coordinate *trans* (α-form), two oxygen atoms of baen should move from the *cis* position to the *trans* position. However, only one oxygen atom should move when the *β*-form is taken.

Two dihalogenated complexes, III and VI, were obtained whenever the complex II was treated with NCS and NBS in a molar ratio of the reactants of 1 : 1 or 1 : 2. However, no diiodinated complex could be isolated because of the contamination of the complex VIII. When iodine monochloride (ICl) was used as the iodinating reagent, the complex II decomposed instantaneously.

The trichloro- and tribromo-substituted complexes were obtained by the two methods shown in the preparative scheme (Fig. 1).

NMR Spectrum of the Complex I. The NMR spectra of the new complexes are shown in Figs. 2, 3, and 4. The numerical data are summarized in Table 1.

The NMR spectrum of the complex I in deuterochloroform exhibits three types of protons, at τ 5.10, 6.97, and 8.15, with the area ratio of 1 : 2 : 6. On the other hand, in carbon tetrachloride I exhibits four types of protons, at τ 5.26, 7.02, 8.20, and 8.25, with the area ratio of 1 : 2 : 3 : 3. Since these spectra resemble that of bis(acetylacetone)ethylenediiminatonickel(II), [Ni(baen)],[4] the peaks were assigned as is shown in Table 1. The difference between the methyl signals in deuterochloroform and in carbon tetrachloride is thought to be due to the difference in the solvation effect; a similar

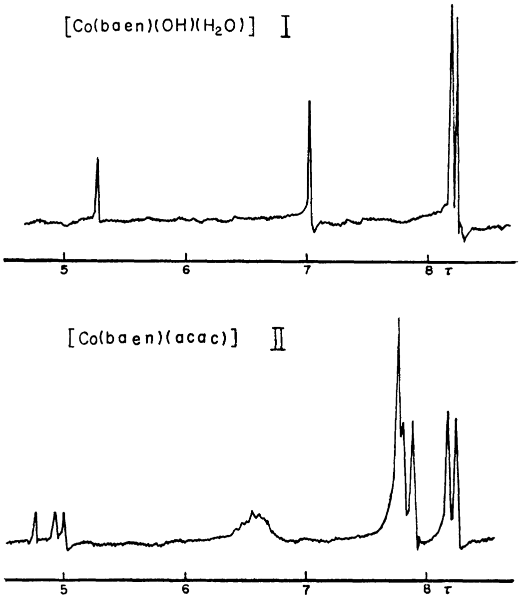


Fig. 2. The NMR spectra of the complexes I and II in CCl_4.

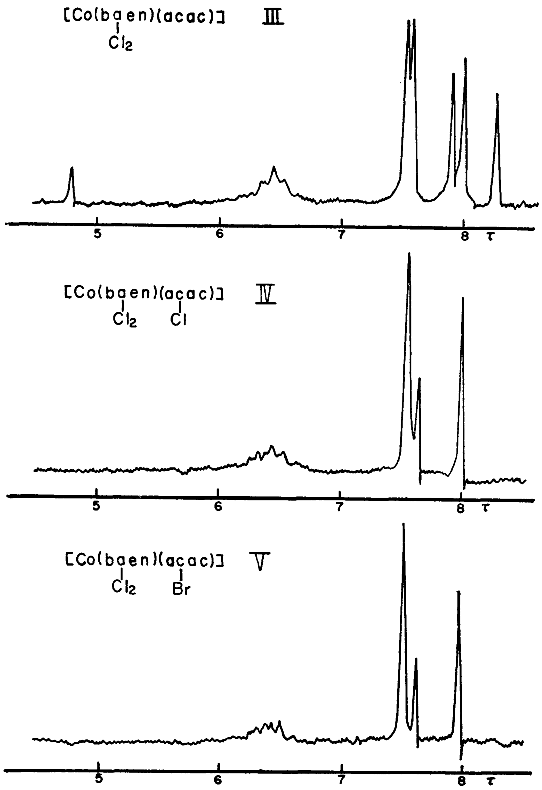


Fig. 3. The NMR spectra of the complexes III, IV, and V in CCl_4.

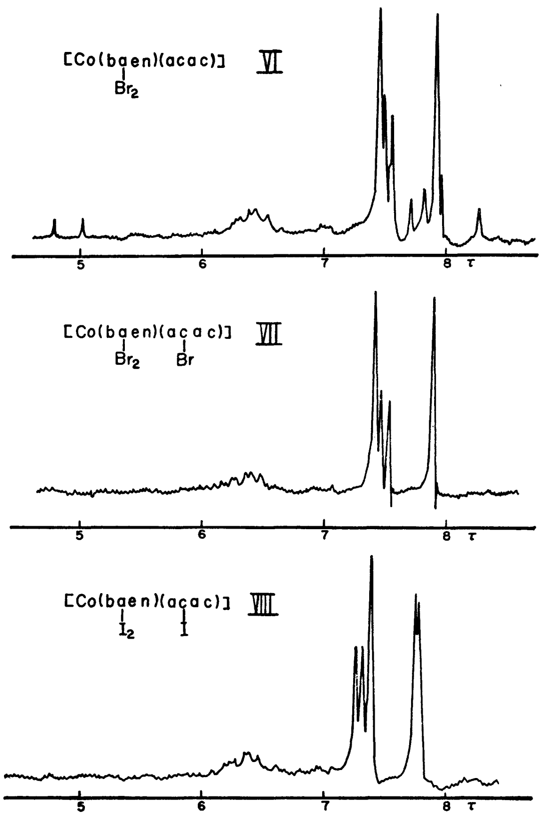


Fig. 4. The NMR spectra of the complexes VI, VII, and VIII in CCl_4.

Table 1. NMR Spectra of the complexes (in τ)

Complex	CH=C (acac)	CH=C (imine)		CH_2	CH_3 B,C_{C-O}	B_{C-N}	C_{C-N}	A_{C-O}	
(I)		5.26 (5.10)		7.02 (6.97)	8.20 (8.15)	8.25			
(II)	4.76 (4.64)	4.92 (4.79)	5.00 (4.81)	6.54* (6.64)	7.77 (7.75)	7.79 (7.68)	8.16 (8.12)	7.89 (7.88)	8.25 (8.23)
(III)	4.76 (4.61)			6.43* (6.38)	7.52 (7.47)	7.57 (7.54)	7.99 (7.93)	7.89 (7.85)	8.25 (8.20)
(IV)				6.41*	7.52	7.52	7.98	7.62	7.98
(V)				6.43*	7.52	7.52	7.97	7.61	7.97
(VI)	4.76	5.00		6.39*	7.43, 7.47, 7.51, 7.54, 7.69, 7.79, 7.91, 7.93, 8.25				
(VII)				6.41*	7.44	7.47	7.91	7.55	7.91
(VIII)				6.36*	7.26 7.32	7.38	7.76	7.38	7.78

( ) represents the spectra in $CDCl_3$. * shows the complicated band.

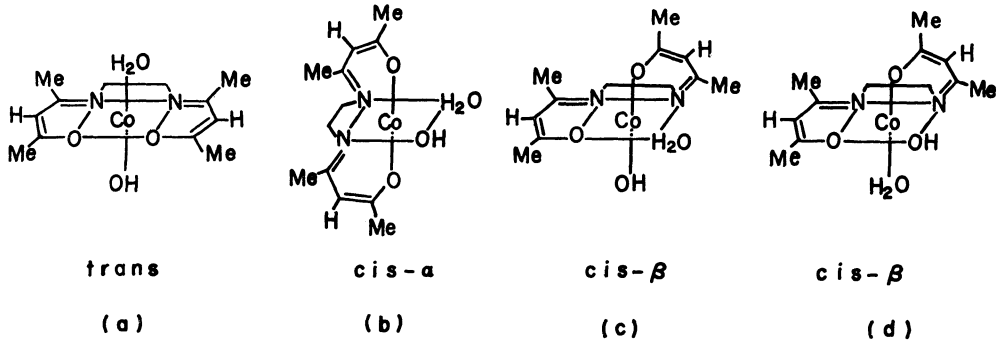
phenomenon has been reported for the NMR spectrum of [Ni(baen)].[4] The assignment of the methyl signals in carbon tetrachloride is as follows: the lower-field signal is due to the methyls adjacent to the C–O groups, and the higher-field signal, to the methyls near the C–N groups,[4] since the methyls adjacent to the C–O groups would be slightly less shielded than those near the C–N groups because of the lower electronegativity of nitrogen than of oxygen.

The peak positions of all the protons were scarcely changed by replacing the metal ion from Ni^{2+} to Co^{3+}. This may be due to the nearly identical ionic radii of the two metal ions.

Though there are four possible geometrical isomers for the complex I, the probable structure may be (a) or (b) in Fig. 5, since the resonance of the ethylene protons shows a single peak.

The coordinated OH and H_2O protons in the complex I did not appear in this measurement (τ−10.0∼10.0), perhaps because of the broadening.

NMR Spectrum of the Complex II. The



trans (a) cis-α (b) cis-β (c) cis-β (d)

Fig. 5. The possible structures of the complex, [Co(baen)(OH)(H_2O)].

NMR spectrum of the complex II shows a rather more complex pattern than that of the complex I. Though two geometrical isomers are possible, as is shown in Fig. 1, this complicated pattern can be safely assigned to that of the β-form, for nine peaks with the area ratio of 1 : 1 : 1 : 4 : 6 : 3 : 3 : 3 : 3, in which the ethylene peak is splitted into the complex pattern, were observed in carbon tetrachloride. If the complex II took the α-form, six peaks, of which the ethylene peak consists of only one signal, should be observed. On the other hand, the β-form would give ten peaks, of which the ethylene peak would consist of more than one signal.

It is known that the signal of the ring proton of the trisacetylacetonatocobalt(II) complex appears at τ 4.63.[1)] This position is apparently located at a field lower than that of the ring protons of imine chelates, such as are seen in the complex I. Therefore, the peak of τ 4.76 in carbon tetrachloride of the complex II may be assigned to the ring proton of the acetylacetone chelate, and the two peaks at τ 4.92 and 5.00 to the ring protons of the two imine chelates. The separation between the chemical shifts of the two imine ring protons is thought to be due to the differences in the solvation and ion-pair effects of the imine rings rather than to the differences in the diamagnetic shielding of the two imine ring protons by the ring-current of the acetylacetone chelate ring, for, from the molecular model, it is known that the ring proton of the B-ring in Fig. 1 is closer to the ethylene bridge than of the C-ring and only very small ring-current, if any, can be expected for the β-diketone complexes.[6)] The separation between the chemical shifts of the ring protons of the acetylacetone ring (A-ring) and the ring protons of the imine rings (B- and C-rings) suggests that the electron density of the γ-position of the A-ring is a little smaller than those of the B- and C-rings and/or that the paramagnetic shielding for the A-ring proton by the ring-current of its own A-ring is a little larger than those in the case of the B- and C-rings. Experimentally, these separations were found to be due mainly to the differences in the electron density at the γ-position between the A-ring and the B- and C-rings, for the chlorination reaction at the imine ring (B- and C-rings) proton precedes the chlorination of the acetylacetone ring (A-ring). The details will be discussed in the next paragraph.

The peak of the ethylene-bridge protons is very complicated; such a complex pattern suggests that the configuration of the complex II is of a β-form, since only one peak is expected for that of the α-form on the basis of the symmetrical property.

The methyl protons show five peaks, with an area ratio of 6 : 3 : 3 : 3 : 3, but evidently the signal at τ 7.77 represents two methyl groups which have not been resolved.

The methyl signals of the complex II were assigned as follows, with the aid of the NMR spectra of the dichlorinated complex, III, and the trichlorinated complex, IV. The signals at τ 7.89 and 8.25 in the complex II were not shifted to the lower field even when the complex II was dichlorinated; they were shifted only when it was trichlorinated. Since the methyl signal of the acetylacetone chelate[1,2)] and the imine chelate of β-diketone[*1] is shifted to the lower field when the ring proton is halogenated, the two signals at τ 7.89 and 8.25 can be assigned to the two methyl groups of the acetylacetone ring. The two peaks, τ 7.79 and 8.18, can be assigned to the two methyl groups near the C–N groups, and the peak at τ 7.77, to the two methyl groups adjacent to the C–O groups of the imine rings, for the methyl protons near the C–N groups will appear at a higher field than that near the C–O groups.[4)] The separation of the chemical shifts between the two methyl groups near the C–N groups is thought to be due to the difference in the steric strain between the two $-CH_2-N=$ groups. Since the steric strain in the C-ring is a little larger than that in the B-ring because of their steric requirement,[7)] since, that is,

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6) R. J. York, W. D. Bonds, B. P. Cotsoradis and R. D. Archer, *Inorg. Chem.*, **8**, 789 (1969).

[*1] This report will be published elsewhere.

7) J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **35**, 567 (1962).

the C-ring takes the meridional form with respect to the two nitrogen atoms and one oxygen atom, while the B-ring takes the facial form, the signal at τ 7.79 can be assigned to the methyl group near the C–N group of the B-ring, and the signal at τ 8.18, to that of the C-ring.

If the ring-current of the β-diketone chelate compounds could be expected to be large enough to be detectable in the NMR spectra, the signals of the methyl groups of acetylacetone chelate should appear at a further lower field than those of the imine chelate of acetylacetone, for the benzenoid resonance of the imine chelate ring can be expected to be smaller than that of the β-diketone chelate ring because of the asymmetric property of the imine ring.[4] Therefore, the paramagnetic shielding of the methyl groups of the imine ring by the ring-current of its own ring is not expected to be larger than that of the acetylacetone ring. However, the peaks of the methyl groups of the acetylacetone ring evidently appear at a higher field than those of the imine rings in the complex II. Therefore, it may be concluded that the ring-current for the β-diketone chelate, if any, is very small, and that the ring-current for the imine chelate of β-diketone, if any, is very small, also. Here, again, the separation of the chemical shifts of the ring protons between the A-ring and the B- and C-ring is confirmed to be due mainly to the difference in the electron density at the γ-positions of the chelate rings.

NMR Spectra of the Complexes III, IV, and V. The dichlorinated complex, III, gives signals at τ 4.76, 6.34, 7.52, 7.57, 7.89, 7.99, and 8.25, with the area ratio of 1 : 4 : 6 : 3 : 3 : 3 : 3 in carbontetrachloride. Evidently, the two ring protons of the imine rings disappears upon dichlorination and only one peak, to be assigned to the ring protons of acetylacetone ring, remains at the same position as the ring proton of acetylacetone ring of the complex II. Therefore, it is clear that the dichlorination occurs at the two imine chelate rings. This means that the two imine-ring protons are more reactive than the acetylacetone-ring proton. This fact also indicates that the electron density at the γ-positions of the imine rings is slightly larger than that of the acetylacetone ring. Therefore, the difference in the chemical shifts of the ring protons between the imine and the acetylacetone rings can be concluded to be due mainly to the difference in the electron density of the carbon atoms (γ-position) where the ring proton is attached.

The methyl signals of the complex III are shifted to a lower field than those of the complex II except the two peaks at τ 7.89 and 8.25. As has been mentioned above, the shift of the methyl signals to the lower field is due to the halogen substitution at the γ-positions of their rings. Therefore, the methyl signals shifted to the lower field by dichlorination can be assigned to the methyl groups of the two imine rings, and the two peaks at τ 7.89 and 8.25, to the two methyl groups of the acetylacetone ring. These assignments are further supported by the NMR data of the trichlorinated complex, IV. The two peaks at τ 7.89 and 8.25 in the complex III are shifted to a lower field by trichlorination and the signal at τ 4.76 assigned to the ring proton of acetylacetone ring disappears.

The methyl protons of the imine rings of the complexes III and IV were also assigned in the same way described above for the complex II. Although the signal at τ 7.57 of the complex III in Fig. 3 seems to have the same intensity as that at τ 7.52, the integration of these peaks indicates that the intensity of the peak at τ 7.57 is half that of the peak at τ 7.52. This is due to the overlap of the skirts of these two peaks. The complex IV shows three methyl peaks, at τ 7.52, 7.62, and 7.98, with an area ratio of 9 : 3 : 6. It is estimated that the signal at τ 7.98 consists of the protons of the two methyl groups, of which one is the methyl group of the acetylacetone ring, and the other, the methyl group near the C–N group of the C-ring. Also, the signal at τ 7.52 is estimated to consist of three methyl groups; two of them are the methyl groups adjacent to the C–O groups of B- and C-rings, while the third is the methyl group near the C–N group of the B-ring.

In the NMR spectra of both complexes, III and IV, the signals of the ethylene-bridge protons are still complicated, as are those of the complex II. This indicates that the configuration of the β-form in the complex II holds also in the chlorinated complexes, III and IV.

The NMR spectrum of the complex V is nearly the same as that of the complex IV. This fact suggests that the substitution of the ring proton by chlorine or bromine atoms does not cause any remarkable change in their NMR spectra.

NMR Spectra of the Complexes VI, VII, and VIII. The NMR spectrum of the complex VI shows a very complicated pattern which is obviously different from that of the complex III. In spite of the dibromination, the signal at τ 5.00 remains, together with the peak at τ 4.76, in the complex VI, while the peak area also remains the same. Furthermore, many elemental analyses of the complex VI invariably showed that the complex VI has two bromines per mole. The possibility of the contamination of the tribrominated complex, VII, to the complex VI during the preparative procedure could thus be ruled out, since the former is less soluble in methanol than the latter and is easily separated from the reaction mixture. Since it has been reported that NBS is stronger than NCS as a halogenating reagent in methanol,[8] it is probable that the bromination occurs at the A-ring proton as well as the B- and

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[8] Y. Fujii, E. Kyuno and R. Tsuchiya, This Bulletin, **42**, 1301 (1969).

C-rings protons. Therefore, it can be estimated that the complex VI is a mixture of the three dibrominated compounds. This estimation is supported by the complicated methyl signals, that is, the peaks at τ 7.91 and 8.25 which are assigned to the two methyl groups of the unsubstituted acetylacetone ring exist together with the two peaks, at τ 7.54 and 7.91, which are assigned to the two methyl groups of the brominated acetylacetone ring by the aid of the NMR spectrum of the complex VII.

The tribrominated complex VII shows a spectrum very similar to that of the complex IV, though the positions of the peaks in the complex VII are shifted to a slightly lower field. Tribromination at γ-positions was confirmed by the disappearance of the three ring protons. The methyl peaks were assigned as in the case of the complex IV.

The triiodinated complex VIII showed a spectrum similar to those of the IV and VII complexes. Triiodination at the γ-positions is also confirmed by the disappearance of the signals of three ring protons. The peaks were assigned as in the case of the complexes IV and VII.

Table 2. IR spectra (in cm^{-1})

Complex	asym. $\nu_{C=C}$	asym. $\nu_{C=O}$ and $\nu_{C=N}$
(I)	1589	1511
(II)	1589	1515
(III)	1579	1520
(IV)	1570	—
(V)	1570	—
(VI)	1564	1515
(VII)	1561	—
(VIII)	1548	—

Infrared, Ultraviolet, and Visible Absorption Spectra. It has been established that the $\nu_{C=C}$ and $\nu_{C=O}$ bands in the region from 1600 to 1500 cm^{-1} of the trisacetylacetonatocobalt(III) complex are shifted to lower-energy site by the substitution at the γ-position and that only one band assigned to the $\nu_{C=C}$ remains in this region.9)

The complex I shows two bands between 1600 and 1500 cm^{-1}, as is shown in Table 2. The band at the higher-energy site can be assigned to the $\nu_{C=C}$ band, and that at the lower-energy site, to the $\nu_{C=N}$ band.10)

The complex II also shows two bands in this region. The band at 1589 cm^{-1} can be assigned to the $\nu_{C=C}$ bands of the acetylacetone ring and the imine ring, which overlap, and the band at 1515 cm^{-1}, to the overlapping bands of $\nu_{C=O}$ and $\nu_{C=N}$. The dihalogenated complexes, III and VI, show two bands in this region, though the intensity of the band at the lower-energy site is small. On the other hand, the trihalogenated complexes show only one band in this region. These bands were assigned as in the case of the trisacetylacetonatocobalt(III), as has been mentioned above. These IR spectra give strong evidence that the complex VI is a mixture of three dibrominated complexes.

The numerical data of the ultraviolet and visible absorption spectra of the new complexes are summarized in Table 3.

The first absorption band is shifted only a little by halogenation. On the other hand, the band near 340 mμ in the complex II is shifted to the lower-energy site by halogenation. The order of this red-shift is Cl<Br<I; this order is that expected for the order of the elongation of the π-system by introducing the halogen atom to the acetylacetone ring and its imine ring.11)

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Table 3. The ultraviolet and visible absorption spectra (in c/s$\times 10^{-13}$)

Complex	ν (log ε)	ν (log ε)	ν (log ε)	ν (log ε)	ν (log ε)
(I)	52.8 (1.88)	66.7 (2.43)	82.2 (3.65) 87.2 (3.67) 100.0 (3.61)	111.1 (4.08)	127.7 (4.53)
(II)	47.6 (2.19)	65.2 (2.50)	88.2 (3.47)	111.1 (3.98)*	122.5 (4.08)
(III)	47.2 (2.30)	63.8 (2.71)	85.7 (3.85)	111.1 (4.27)*	120.0 (4.44)
(IV)	47.2 (2.61)	63.8 (3.04)	84.5 (4.12)	111.1 (4.48)*	125.0 (4.68)
(V)	47.6 (2.61)	63.8 (3.07)	88.2 (4.17)	111.1 (4.46)*	125.0 (4.66)
(VI)	47.2 (2.27)	63.8 (2.71)	87.0 (3.77)	111.1 (4.14)*	125.0 (4.34)
(VII)	47.2 (2.52)	63.8 (2.91)	83.3 (3.95)	111.1 (4.27)*	125.0 (4.49)
(VIII)	47.2 (2.32)	63.8 (2.91)	82.6 (3.80)	111.1 (4.32)*	125.0 (4.62)

* represents the shoulder.

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