BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 283—285(1972)

# An NMR Study of Metal Complexes Containing Acetylacetone and Related Compounds. II. The Preparation and Structure of Mixed Cobalt(III) Complexes Containing Acetylacetone and Amino Acids

Yuki Fujii and Toshio Ejiri

*Department of Chemistry, Ibaraki University, Bunkyo-cho, Mito, Ibaraki*

(Received May 7, 1971)

Many reports have been published on the NMR spectra of tris-type $\beta$-diketonatocobalt(III) complexes.[1–3] Recently, bis-type acetylacetonatocobalt(III) complexes have also been prepared. Their NMR spectra have been studied and their geometrical isomers assigned.[4–8]

In this paper, we will report the preparations of mixed cobalt(III) complexes containing one molecule of the acetylacetone anion and two molecules of the amino acid anion, and will discuss the relation between the structures of mono-type acetylacetonatocobalt(III) complexes and their NMR spectra.

## Experimental

*Preparation of the Complexes.* *1)* cis(N)cis(O)-*Bisglycinatoacetylacetonatocobalt(III) Monohydrate,* cis(N) cis (O)-*[Co(gly)$_2$(acac)]$\cdot$H$_2$O (I)*: Sodium dinitrobisacetylacetonatocobalt (III)[4] (8.0 g, 0.014 mol) was dissolved in 200 m*l* of water, and then methanol (40 m*l*), glycine (2.0 g, 0.027 mol) neutralized with potassium hydroxide (0.86 g) in 30 m*l* of water, and activated charcoal (2.0 g) were added to the solution in this order. The mixture was heated at about 70°C for ten minutes, the activated charcoal was filtered off, and the filtrate was concentrated to about 40 m*l*; the trisacetylacetonatocobalt(III) thus deposited was then filtered off. When acetone (100 m*l*) was added to the filtrate, reddish-purple crystals were separated out. They were subsequently recrystallized from 33% acetone. Yield, about 1.5 g (32%). Found: C, 35.23; H, 5.65; N, 9.00%. Calcd for $C_9H_{15}CoN_2O_6\cdot H_2O$: C, 35.07; H, 5.57; N, 9.09%.

*2)* cis(N)trans(O)-*Bisglycinatoacetylacetonatocobalt(III) Monohydrate,* cis(N)trans(O)-*[Co(gly)$_2$(acac)]$\cdot$H$_2$O (II)*: Trisacetylacetonatocobalt(III) (3.6 g, 0.01 mol) was dissolved in 200 m*l* of methanol. Glycine (1.5 g, 0.02 mol) neutralized with potassium hydroxide (1.2 g) in 50 m*l* of water and

---

[1] R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, **84**, 2023 (1962); **85**, 500 (1963).

[2] R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).

[3] J. P. Collman and J. Y. Sun, *ibid.*, **4**, 1273 (1965).

[4] L. J. Boucher and J. C. Bailar, Jr, *J. Inorg. Nucl. Chem.*, **27**, 1093 (1765).

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

[6] B. P. Cotsoradis and R. D. Archer, *ibid.*, **6**, 800 (1967).

[7] R. J. York. W. D. Bonds, Jr., B. P. Cotsoradis, and R. D. Archer, *ibid.*, **8**, 789 (1969).

[8] L. J. Boucher and N. G. Paeg, *ibid.*, **9**, 418 (1970).

activated charcoal (1.0 g) were added, and the mixture was heated at about 60°C for fifteen minutes. The activated charcoal was then filtered off, and the filtrate was concentrated to about 30 m*l* by evaporating the solvent under reduced pressure. When acetone (100 m*l*) was added to the solution, reddish-purple crystals were separated out. (These crystals were a 1 : 2 mixture of *cis(N)cis(O)* and *cis(N)trans(O)* isomers.) The crystals were dissolved in 50 m*l* of water, and the solution was concentrated slowly by evaporating the solvent to about 25 m*l*. When the solution was allowed to stand for a day, only the *cis(N)trans(O)* isomer was separated out. The crystals were subsequently washed with water and methanol. Yield, about 0.5 g (15%). Found: C, 35.12; H, 5.37; N, 9.25%. Calcd for $C_9H_{15}CoN_2O_6 \cdot H_2O$: C, 35.07; H, 5.57; N, 9.09%.

*3)* cis(N)trans(O)-*Bis*-L-*alaninatoacetylacetonatocobalt(III) Dihydrate,* cis(N)trans(O)-[*Co(*L-*ala)*$_2$*(acac)*] · *2*$H_2O$ *(III)*: This complex was prepared by the same method as was the complex I. Yield, about 2.0 g (40%). The reaction between trisacetylacetonatocobalt(III) and L-alanine also gave only the *cis(N)trans(O)* isomer. Yield, about 1.2 g (33%). Found: C, 37.35; H, 6.68; N, 7.89%. Calcd for $C_{11}H_{19}CoN_2O_6 \cdot 2H_2O$: C, 37.29; H, 6.56; N, 7.91%.

*4) Potassium Bis(acetylacetoneglyciniminato)cobalt(III) Tetrahydrate,* trans(N)-*K*[*Co(acacgly)*$_2$]·*4*$H_2O$ *(IV)*: A solution of 19.5 g of cobalt(II) chloride hexahydrate in 20 m*l* of water was added to a solution of 12 g of acetylacetone neutralized with potassium hydroxide (6.6 g) and 17.8 g of glycine in 100 m*l* of water. The mixed solution was oxidized with a hydrogen peroxide solution and then warmed at 50—60°C for one hour. The solution was concentrated under reduced pressure to a volume of 30 m*l*; the trisacetylacetonatocobalt(III) and potassium chloride thus deposited were then filtered off. When the resulting solution was cooled to 0°C, reddish-brown crystals were separated out. They were recrystallized from water. Yield, about 4.0 g (10%). Found: C, 35.23; H, 5.52; N, 5.94%. Calcd for $C_{14}H_{18}CoN_2O_6 \cdot 4H_2O$: C, 35.00; H, 5.47; N, 5.83%.

*Measurements.* The IR spectra were recorded with a Hitachi EPI-S2 infrared abosrption spectrophotometer by using the potassium bromide disk. The visible and ultraviolet abosorption spectra were measured with a Hitachi EPS-3 spectrophotometer in water. 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 deutrated water by using NaTMS as the internal reference.

## Results and Discussion

*Infrared Absorption Spectra.* The main bands of the IR spectra are listed in Table 1. All the complexes show an asym. $\nu_{COO}$ band between 1630 and 1680 cm$^{-1}$, and $\nu_{C=C}$ and $\nu_{C=O}$ (and $\nu_{C=N}$ for the complex IV) bands between 1500 and 1570 cm$^{-1}$. Thus, we can conclude that all the carboxylate groups of the amino acid in Complexes I to IV are coordinated to the cobalt(III) ion,[9] and also that the acetylacetonate anions are chelated to the cobalt(III) ion.[10] Complexes I, II, and III give the bands of $\nu_{NH_2}$ and $\delta_{NH_2}$, but Complex IV does not. Therefore, in the case of Complex IV, the formation of the Schiff-base between acetylacetone and glycine is confirmed.

TABLE 1. INFRARED ABSORPTION SPECTRA (in cm$^{-1}$)

| Complex | $NH_2$ str. | COO asym. str. | $NH_2$ bend. | C=C str. | C=O str. |
|---|---|---|---|---|---|
| I | 3260<br>3140 | 1675<br>1640 | 1586 | 1566 | 1512 |
| II | 3280<br>3150 | 1670<br>1640 | 1586 | 1565 | 1515 |
| III | 3250 | 1665<br>1637 | 1595 | 1567 | 1525 |
| IV | | 1630 | | 1592 | 1502<br>(C=N str.) |

TABLE 2. VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA (in c/s × 10$^{-13}$)

| Complex | $\nu_{max}$ (log $\varepsilon$) | $\nu_{sh}$ (log $\varepsilon$) | $\nu_{max}$ (log $\varepsilon$) |
|---|---|---|---|
| I | 55.6 (2.19) | 78.8 (2.37) | 92.2 (3.61) |
| II | 56.7 (2.22) | 78.8 (2.46) | 92.0 (3.59) |
| III | 57.1 (2.02) | 78.8 (2.30) | 92.0 (3.57) |
| IV | 47.5 (1.77) (sh),<br>57.4 (2.47) | | 90.6 (3.97) |

*Electronic Absorption Spectra.* The numerical values of the electronic absorption spectra are listed in Table 2. The first abosrption bands of Complexes I, II, and III appear at about 56 × 10$^{13}$ c/s, and their positions are nearly equal to those of the bisglycinatooxalatocobalt(III) complexes.[11] Since the first bands of Complexes I, II, and III show no splitting, these complexes can be assigned to the *cis(N)*-form structure.

Complex IV, on the other hand, shows a split first absorption band; therefore, a *trans(N)*-form structure can be assigned to this complex.

*NMR Spectra.* The NMR spectra of the complexes are shown in Figs. 1 and 2, while their numerical values are listed in Table 3.

From these NMR spectra, it can be concluded that Complexes I and II have *cis(N)cis(O)* and *cis(N)-trans(O)* forms respectively. Moreover, it can be concluded that Complex III has the *cis(N)trans(O)* form. In the cases of the bisglycinatocobalt(III) complexes, it is confirmed that the *cis(N)cis(O)* isomer shows a $CH_2$ signal constructed of two peaks, while the *cis(N)-trans(O)* isomer gives one peak.[11] Also it is shown that the difference between the *cis(N)cis(O)* and *cis-(N)trans(O)* structures is more clearly distinguished by the methyl signals of the acetylacetonate group.

Complex IV shows one C=CH, one $CH_2$, and two $CH_3$ peaks with relative intensities of 1 : 2 : 3 : 3. This

TABLE 3. PMR SPECTRA (in $\tau$)

| Complex | C=CH | $CH_2$ | $CH_3$(acac) |
|---|---|---|---|
| I | 4.22 | 6.45<br>6.65 | 7.71<br>7.92 |
| II | 4.30 | 6.34 | 7.92 |
| III | 4.25 | $\left.\begin{matrix}5.91\\6.03\\6.15\end{matrix}\right\}$ CH(ala) | 7.93<br>$\left.\begin{matrix}8.43\\8.55\end{matrix}\right\}$ $CH_3$(ala) |
| IV | 5.39 | 6.50 | 7.58<br>8.33 |

---

9) T. Sakaguchi and K. Ueno, "Metal Chelates," Vol. II, Nankodo, Tokyo (1963), p. 43.

10) K. Nakamoto, P. J. MacCarthy, A. Ruby, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 1066 (1961).

11) N. Matsuoka, J. Hidaka, and Y. Shimura, This Bulletin, **40**, 1868 (1967).

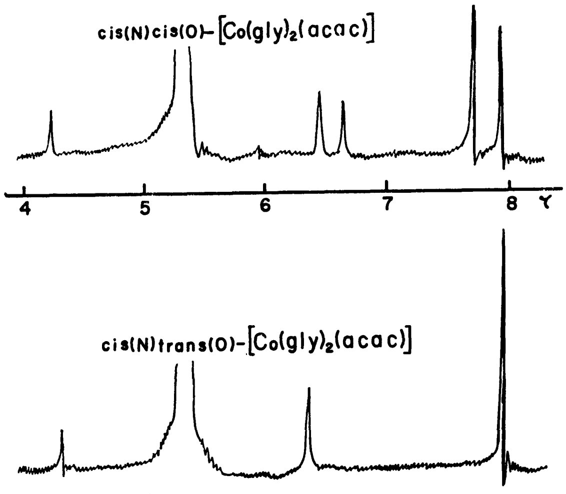

Fig. 1. PMR spectra of the complexes.

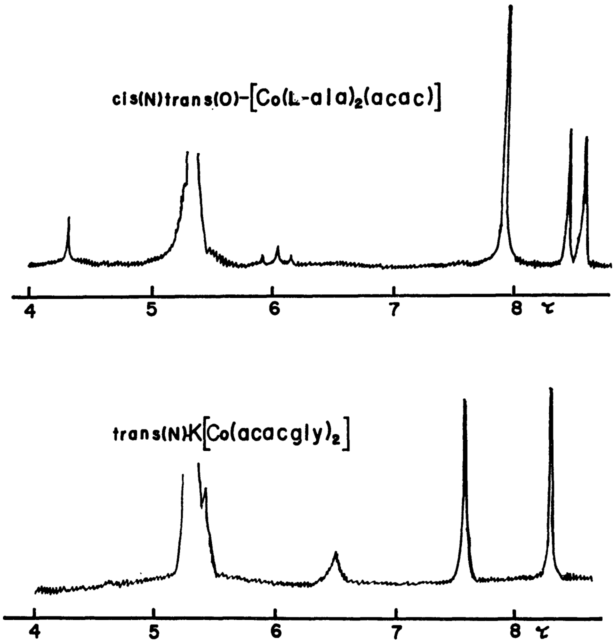

Fig. 2. PMR spectra of the complexes.

spectral pattern clearly implies that Complex IV is a Schiff-base complex in which acetylacetone and glycine are condensed. This fact has also been confirmed by studying the IR spectrum. It is assumed that the formation of the schiff-base complex may be the cause of the difficulty of preparing the *trans(N)cis(O)* isomer.