  Bull. Chem. Soc. Jpn., 60, 539—543 (1987) 

# Nocovalent Interactions in Metal Complexes. 14.[1] Proton NMR Spectroscopic Investigation on Stereoselectivity in Cobalt(III) Complexes of Various 3-Substituted 1-Phenyl-1,3-propanediones

Michio NAKAMURA, Hisashi ŌKAWA,* Tasuku ITO,[†,#1] Masako KATO,[†,#2] and Sigeo KIDA[#3]
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812
[†]Department of Applied Molecular Science, Institute for Molecular Science,
Okazaki National Research Institute, Okazaki 444
(Received August 6, 1986)

1 : 3-Cobalt(III) complexes of 3-substituted 1-phenyl-1,3-propanediones ($C_6H_5$-CO-$CH_2$-CO-R) have been synthesized, and their stereoselectivities were studied with 400 MHz proton NMR spectroscopy. When the substituent (R) was ethyl, propyl, isopropyl, butyl, or isobutyl, the complexes were obtained in a mixture of fac and mer isomers with the fac/mer ratio of 1/3, demonstrating statistical distribution. When the substituent was *t*-butoxymethyl or cyclohexyloxymethyl the fac isomer was predominantly formed. The stereoselectivity in the geometrical isomer formation of the complexes was ascribed to the interligand CH/$\pi$-interaction occuring between the R group and the phenyl ring. The stereoselectivities of the complexes [Co(*l*-moba-X)$_3$] (*l*-moba-X$^-$=4-(*l*-menthyloxy)-1-(*p*-X-phenyl)-1,3-butanedionate ion; X=H, Br, $CH_3$) were also examined by means of $^1$H NMR spectroscopy and compared with the CD spectral result previously reported.

Previously we reported the stereoselective formation of the fac-$\Delta$ isomer of tris{4-(*l*-menthyloxy)-1-phenyl-1,3-butanedionato}M(III) complexes, [M(*l*-moba)$_3$] (M=Co, Cr, Mn) (Fig. 1(a); X=H).[2] This stereoselectivity was presumed to be due to the intramolecular, interligand CH/$\pi$-interaction[3] operating between the phenyl group and the *l*-menthyl group (Fig. 2). This presumption is supported by the facts that (1) the stereoselectivity in tris{4-(*l*-menthyloxy)-1-(2-naphthyl)-1,3-butanedionato}M(III) [M(*l*-mona)$_3$] (Fig. 1(b)) is higher than that of [Co(*l*-moba)$_3$] because of the larger $\pi$-system of the naphthyl group compared with the phenyl group[4] and (2) the stereoselectivity of [M(*l*-moba-Br)$_3$], [M(*l*-moba)$_3$], and [M(*l*-moba-Me)$_3$] (see Fig. 1(a)) is enhanced in this order because the $\pi$-electron density of the ring increases in the order 4-Br$C_6H_4$<$C_6H_5$<4-$CH_3C_6H_4$.[5]

So far we have inspected the stereoselectivities of the complexes based on circular dichroism induced at d-d transition bands. In this study we aimed to obtain direct evidences for the stereoselectivities of cobalt(III) complexes by means of high-resolution (400 MHz) proton NMR spectroscopy. We have synthesized 1 : 3-cobalt(III) complexes of various 3-substituted 1-phenyl-1,3-propanediones (Fig. 1(c)). The stereoselectivity in the formation of geometrical isomers (fac and mer) of the complexes was examined by $^1$H NMR spectroscopy and discussed in terms of intramolecular, interligand interaction. Further, the stereoselectivities of [Co(*l*-moba-X)$_3$] (X=H, Br, Me) were examined by means of $^1$H NMR spectroscopy, and compared with the CD spectral result previously reported.[4]

3-Substituted 1-phenyl-1,3-propanediones used in

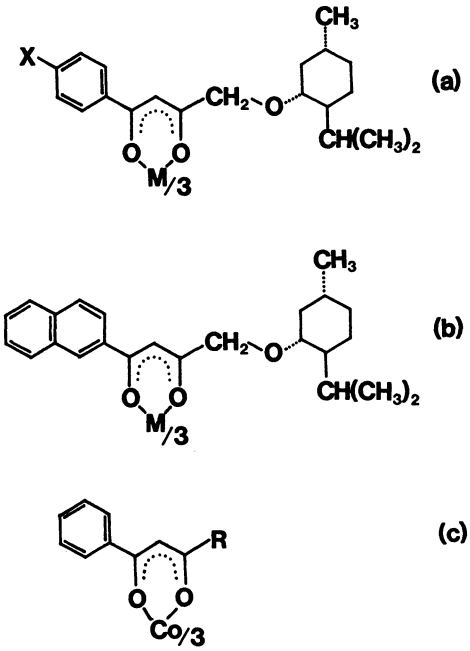


Fig. 1. Chemical structures of (a) [M(*l*-moba-X)$_3$] (X=H, Br, $CH_3$), (b) [M(*l*-mona)$_3$], and (c) [Co(L-R)$_3$].

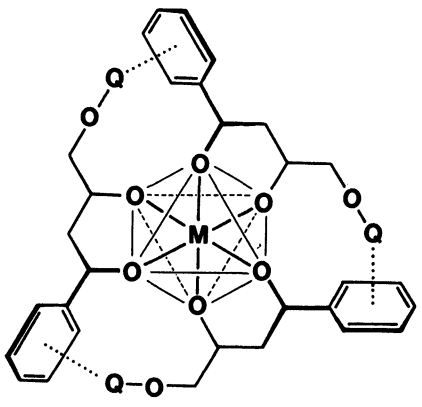


Fig. 2. Schematical representation of interligand CH/$\pi$-interaction in [M(*l*-moba)$_3$] (Q=*l*-menthyl).

[#1] Present address: Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980.
[#2] Present address: Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606.
[#3] Present address: Coordination Chemistry Laboratories, Institute for Molecular Science, Okazaki National Research Institute, Okazaki 444.

Table 1. Abbreviations of 3-Substituted 1-Phenyl-1,3-diones[a)]

| R | X | Ligand |
|---|---|---|
| $-\overset{\alpha}{C}H_2\overset{\beta}{C}H_3$ | H | H(L-Et) |
| $-\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_3$ | H | H(L-*n*Pr) |
| $-\overset{\alpha}{C}H(\overset{\beta}{C}H_3)_2$ | H | H(L-*i*Pr) |
| $-\overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3$ | H | H(L-*n*Bu) |
| $-\overset{\alpha}{C}H_2\overset{\beta}{C}H(\overset{\gamma}{C}H_3)_2$ | H | H(L-*i*Bu) |
| $-\overset{\alpha}{C}H_2$-C$_6$H$_5$ | H | H(L-Bz) |
| $-\overset{\alpha}{C}H_2O\overset{\delta}{C}(CH_3)_3$ | H | H(L-BuO) |
| $-\overset{\alpha}{C}H_2O$-C$_6$H$_4$ (1,2,3,4,5,6) | H | H(L-CyO) |
| $-\overset{\alpha}{C}H_2O$-C$_6$H$_3$(isopropyl) (1,2,3,4,5,6) | H | H(*l*-moba) |
| $-\overset{\alpha}{C}H_2O$-C$_6$H$_3$(isopropyl) | Br | H(*l*-moba-Br) |
| $-\overset{\alpha}{C}H_2O$-C$_6$H$_3$(isopropyl) | $CH_3$ | H(*l*-moba-Me) |

a) See Fig. 1.

this study are given in Table 1, together with their abbreviations.

## Experimental

**Materials.** Methyl ethyl ketone, methyl *n*-propyl ketone, methyl *i*-propyl ketone, methyl *n*-butyl ketone, methyl *i*-butyl ketone, acetophenone, *p*-bromoacetophenone, and *p*-methylacetophenone were purchased from Nakarai Chemical Co. *l*-Menthyloxyacetic acid was purchased from Tokyo Kasei Chemical Co. *t*-Butoxyacetic acid and cyclohexyloxyacetic acid were synthesized by the reaction of chloroacetic acid with *t*-butyl alcohol and cyclohexanol, respectively.[6)] Ethyl benzoate, ethyl *t*-butoxyacetate, and ethyl cyclohexyloxyacetate were synthesized by the esterification of the corresponding carboxylic acids.

**Preparation.** 3-Substituted 1-phenyl-1,3-propanediones (generally represented by H(L-R)) were synthesized by the Claisen condensation reaction[7)] between corresponding ester and ketone in the presence of sodium hydride as the base. The synthetic methods for H(*l*-moba-X) (X=H, Br, Me) have been described in the preceding papers.[2,5)]

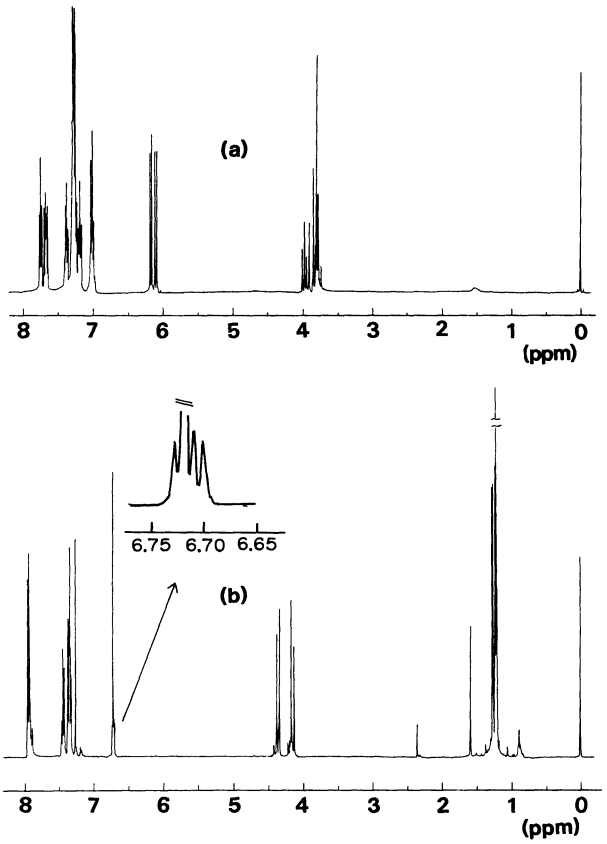


Fig. 3. Proton NMR spectra of (a) [Co(L-Bz)$_3$] and (b) [Co(L-BuO)$_3$].

Cobalt(III) complexes were obtained by the reaction of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ and H(L-R)), in a way similar to that for tris(benzoylacetonato)cobalt(III).[8)] All the [Co(L-R)$_3$] complexes were obtained as green oily substances. They were purified by eluting through an alumina column (10 mm×100 mm) and identified by $^1$H NMR spectra.

**Measurements.** $^1$H NMR spectra were measured on a JEOL Fourier Transform NMR Spectrometer JNM GX-400 in $CDCl_3$. Tetramethylsilane was used as an internal standard.

## Results and Discussion

For 1 : 3-cobalt(III) complexes of unsymmetrical 1,3-diketones, there are two geometrical isomers, fac and mer. The statistical ratio for the fac/mer isomers is 1/3. In the fac isomer three ligands are equivalent, whereas in the mer isomer no ligands are equivalent to each other.[9)] Therefore, in $^1$H NMR spectra of tris(1,3-diketonato)cobalt(III) complexes, the methine proton in the chelate ring, for example, should be observed as four singlets with the same intensity (one from fac isomer and three from mer isomer) if there is no stereoselectivity in the formation of the complexes. When the interligand CH/$\pi$-interaction operates in the molecule to produce predominantly the fac isomer,

Table 2. $^1$H NMR Spectral Data for 3-Substituted 1-Phenyl-1,3-propanediones and Their Cobalt(III) Complexes[a)]

| | Ligand δ/ppm | Complex δ/ppm |
|---|---|---|
| H(L-Et) | met: 6.16(s)<br>α: 2.45(qa)<br>β: 1.20(t) | met: 6.19 6.22 6.23 6.24[b)]<br>α: 2.52—2.65(m)<br>β: 1.09—1.19(m) |
| H(L-*n*Pr) | met: 6.16(s)<br>α: 2.39(t)<br>β: 1.71(qa)<br>γ: 0.99(t) | met: 6.18 6.20 6.21 6.22[b)]<br>α: 2.43—2.65(m)<br>β: 1.56—1.71(m)<br>γ: 0.79—0.96(m) |
| H(L-*i*Pr) | met: 6.19(s)<br>α: 2.61(mc)<br>β: 1.22(d) | met: 6.21 6.23 6.27 6.30[b)]<br>α: 2.81—2.86(m)<br>β: 1.10—1.15(m) |
| H(L-*n*Bu) | met: 6.17(s)<br>α: 2.15(t)<br>β: 1.65(mc)<br>γ: 1.40(mc)<br>δ: 0.94(t) | met: 6.19 6.20 6.21 6.22[b)]<br>α: 2.35—2.68(m)<br>β: 1.56—1.64(m)<br>γ: 1.18—1.39(m)<br>δ: 0.68—0.92(m) |
| H(L-*i*Bu) | met: 6.15(s)<br>α: 2.28(d)<br>β: 2.17(mc)<br>γ: 0.99(d) | met: 6.15 6.16 6.17 6.19[b)]<br>α: 2.26—2.58(m)<br>β: 2.10—2.14(m)<br>γ: 0.76—0.97(m) |
| H(L-Bz) | met: 6.12(s)<br>α: 3.73(s) | met: 6.08 6.11 6.16 6.19<br>α: 3.73—4.01(m) |
| H(L-BuO) | met: 6.60(s)<br>α: 4.08(s)<br>δ: 1.28(s) | met: 6.72 (6.70 6.71 6.73)[c)]<br>α: 4.12 4.16 4.33 4.37[d)]<br>δ: 1.21 (1.23 1.25 1.27)[c)] |
| H(L-CyO) | met: 6.57(s)<br>α: 4.17(s) | met: 6.78 (6.77 6.79 6.80)[c)]<br>α: 4.22 4.25 4.42 4.46[d)] |
| H(*l*-moba) | met: 6.56(s)<br>α: 4.16(qa)[d)]<br>2-iPr: 0.95(d), 0.82(d)<br>5-Me: 0.93(d) | met: 6.69 6.70 6.73<br>α: 4.14—4.51(m)<br>$CH_3$: 0.73—0.91(m) |
| H(*l*-moba-Br) | | met: 6.63 6.64 6.65 6.67<br>α: 4.06—4.47(m)<br>$CH_3$: 0.72—0.93(m) |
| H(*l*-moba-Me) | | met: 6.66<br>α: 4.13—4.54(m)<br>$CH_3$: 0.72—0.95(m) |

a) See Fig. 1 and Table 1. Abbreviations: met=methine proton, s=singlet, d=doublet, t=triplet, qa=quartet, qi=quintet, mc=multiplet center, $CH_3$=three methyl groups of the *l*=menthyl group. b) Four peaks with nearly the same intensity. c) Weak peaks in parentheses. d) AB quartet.

only one singlet of the methine signal (or one intense and three weak singlets) should be observed. Thus, the stereoselectivity in tris(1,3-diketonato)cobalt(III) complexes can be inspected by the number of the methine proton signals and their relative intensities.

Each $^1$H NMR spectrum of the free ligands H(L-R) shows a singlet peak in the 6.1—6.7 ppm which can be assigned to the methine proton on the chelate ring. The integrated intensity of this signal corresponds to one proton, clearly indicating that the diketones assume the enol form. The assignment of main $^1$H NMR signals of the ligands are given in Table 2.

As shown in Fig. 3(a), the spectrum of [Co(L-Bz)$_3$] shows four singlets with the equal intensity in the 6.08—6.18 ppm region, attributable to the methine protons. Evidently the fac/mer ratio is the statistical one, indicating no stereoselectivity in this case. A similar $^1$H NMR spectral feature (four methine signals)

was observed for [Co(L-Et)$_3$], [Co(L-*n*Pr)$_3$], [Co(L-*i*Pr)$_3$], [Co(L-*n*Bu)$_3$], and [Co(L-*i*Bu)$_3$] (Table 2). On the other hand, the NMR spectrum of [Co(L-BuO)$_3$] showed a strong peak at 6.72 ppm attributable to the methine proton of the fac isomer, together with three very weak peaks at 6.70, 6.71, and 6.73 ppm attributable to the methine proton of the mer isomer (Fig. 3(b)). The methine proton intensity of the fac isomer is about 10 times that of each peak for the mer isomer, indicating the fac/mer ratio of ca. 10/3 for this complex. The fac/mer ratio was also estimated by the proton signal intensities of *t*-butyl groups; the 1.21 ppm signal attributable to the fac isomer is about 10 times as strong as the signals at 1.23, 1.25, and 1.27 ppm attributable to the mer isomer. [Co(L-CyO)$_3$] also showed a similar spectral pattern in the methine signal region, demonstrating the predominant formation of the fac isomer (Table 2). The fac/mer ratio for this complex was estimated at ca. 3 from the methine peak intensities. The stereoselectivities found for [Co(L-BuO)$_3$] and [Co(L-CyO)$_3$] may be attributed to the intramolecular, interligand CH/$\pi$-interaction as supposed for [M(*l*-moba-X)$_3$][2,5] and [M(*l*-mona)$_3$][4] (see Fig. 2).

The Dreiding model considerations suggest that the substistuent R with a carbon chain longer than two-carbon chain ($C_2$) may come into contact with the neighbouring phenyl ring in [Co(L-R)$_3$] but such a contact is not feasible in the complex with the substituent of $C_2$ chain. No stereoselectivity in [Co(L-Et)$_3$] and [Co(L-*i*Pr)$_3$], therefore, is easily understandable. However, [Co(L-*n*Pr)$_3$], [Co(L-*n*Bu)$_3$], [Co(L-*i*Bu)$_3$], and [Co(L-Bz)$_3$] also showed no stereoselectivity in spite of their substituent longer than $C_2$ chain. In the case of [Co(L-Bz)$_3$], the phenyl and the benzyl rings cannot stack with each other from the steric requirement of the molecule, and this may be a reason for no stereoselectivity of this complex. In contrast to the above complexes, [Co(L-BuO)$_3$] and [Co(L-CyO)$_3$] showed a high stereoselectivity.

It is not straightforward to explain the marked difference in stereoselectivities between the two classes, ([Co(L-*n*Pr)$_3$], [Co(L-*n*Bu)$_3$], and [Co(L-*i*Bu)$_3$]) and ([Co(L-BuO)$_3$] and [Co(L-CyO)$_3$]). At the moment we only point out two geometrical features which might relate to the different stereoselectivity between the two classes; (1) the latter class contains the ether group at the $\beta$-position of the substituent whereas the $\beta$-group for the former class is the methylene group, and (2) the latter class contains an inflexible hydrophobic group (*t*-butyl or cyclohexyl) in the R substituent whereas former class contains a rather flexible group in the substituent.

Proton NMR technique was applied to the analysis of the stereoselectivities of [Co(*l*-moba-Br)$_3$], [Co(*l*-moba)$_3$], and [Co(*l*-moba-Me)$_3$]. The spectra in the methine proton region are given in Fig. 4. In the spectra of [Co(*l*-moba-Br)$_3$] and [Co(*l*-moba)$_3$], four

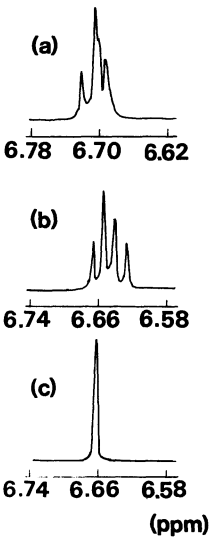


Fig. 4. NMR spectra (methine proton region) of (a) [Co(*l*-moba)$_3$], (b) [Co(*l*-moba-Br)$_3$], and (c) [Co(*l*-moba-Me)$_3$].

signals were observed. The result clearly indicates that each complex obtained is not of a pure isomer but a mixture of isomers. Since our CD spectral investigations have shown the predominant formation of the fac-isomer for these complexes,[5] the highest methine signal (6.65 ppm of [Co(*l*-moba-Br)$_3$] and 6.71 ppm of [Co(*l*-moba)$_3$]) may be assigned to this isomer. In the spectrum of [Co(*l*-moba-Me)$_3$], on the other hand, only one methine signal was observed at 6.66 ppm, clearly demonstrating that the fac-$\Delta$ isomer was selectively formed in this case. It is revealed from the present NMR spectral study that the stereoselectivity of [Co(*l*-moba-Br)$_3$], [Co(*l*-moba)$_3$], and [Co(*l*-moba-Me)$_3$] increases in this order, in accordance with the CD spectral result previously reported.[4]

It should be noted that the circular dichroism of [Co(*l*-moba-Me)$_3$], which is proved to be optically pure in this study, is 2.5 times as intense as that of optically pure [Co(acac)$_3$].[10,11] Judging from the fact that optical activity arising from the vicinal effect is at least two orders of magnitude smaller than that from the configurational effect,[12] it is suggested that the interligand CH/$\pi$-interaction enhances the distortion about the three-fold axis of the [Co(*l*-moba-Me)$_3$] molecule and thence increases the optical activity at the metal.

This work was supported by the Joint Studies Program (1984—1985) of the Institute for Molecular Science.

## References

1) Part 13: H. Ōkawa, M. Nakamura, Y. Shuin, and S. Kida, *Bull. Chem. Soc. Jpn.*, **59**, 3657 (1986).

2) H. Ōkawa, K. Ueda, and S. Kida, *Inorg. Chem.*, **21**, 1594 (1982).

3) M. Nishio, *Kagaku No Ryoiki*, **31**, 998 (1977). The

weak interaction between an aromatic ring and proton of an alkyl or alicyclic group is designated as CH/$\pi$-interaction.

4) M. Nakamura, H. Ōkawa, and S. Kida, *Inorg. Chim. Acta*, **96**, 111 (1984).

5) M. Nakamura, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **58**, 3377 (1985).

6) M. T. Leffler and A. E. Calkins, *Org. Synth.*, Col. Vol. III, p. 545.

7) F. W. Swamer and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 1352 (1950).

8) H. F. Bauer and W. C. Dinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

9) A. Y. Girgis and R. C. Fay, *J. Am. Chem. Soc.*, **92**, 7061 (1970).

10) R. B. Von Dreele and R. C. Fay, *J. Am. Chem. Soc.*, **93**, 4936 (1971).

11) R. R. Judkins and D. J. Royer, *Inorg. Chem.*, **13**, 945 (1974).

12) T. Yasui, J. Fujita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **42**, 2081 (1969).