BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2459—2464 (1972)

An NMR Study of Metal Complexes Containing Acetylacetone and Related Compounds. III. The Preparation and Determination of the Configurations of Cobalt(III) Complexes Containing *N,N'*-Ethylenebis(acetylacetonimine) and *N,N'*-Ethylenebis(salicylideneimine)

Yuki Fujii, Akio Osawa, Yoichiro Furukawa, Fujio Ebina, and Sozo Takahashi*
Department of Chemistry, Ibaraki University, Bunkyo-cho, Mito, Ibaraki
**Department of Chemistry, Ibaraki Technical College, Fukayatsu, Nakane, Katsuta, Ibaraki*

(Received December 14, 1971)

A series of *cis-β*-form cobalt(III) complexes containing *N,N'*-ethylenebis(acetylacetonimine) dianion (baen) or *N,N'*-ethylenebis(salicylideneimine) dianion (salen) were prepared—*cis-β*-[Co(X)(Y)] and *cis-β*-[Co(X)(Z)]ClO_4 (where X = baen or salen, Y = anions of acetylacetone, benzoylacetone, 8-hydroxyquinoline, and Z = ethylenediamine, 1,10-dipyridyl, 1,10-phenanthroline). The synthetic methods and characterization data are given. Also prepared were a series of *trans*-form cobalt(III)-bean complexes—*trans*-[Co(X)$(A)_2$]ClO_4 and *trans*-K[Co(X)$(NO_2)_2$] where X = baen, and A = ammonia, methylamine, pyridine, aniline). The isolation of only *cis-β*-form complexes in reactions between [Co(X)$(H_2O)_2$] and the bidentate ligands contrasts with the isolation of only *trans*-form ones in those between [Co(X)$(H_2O)_2$] and the monodentate ligands. This result was explained in terms of the relative stabilities of the three configurations of the coordinated baen and salen. On the basis of the configurational analysis, the relative stabilities of the three configurations were determined to be *trans*-planar form > *cis-β* form > *cis-α* form.

Cobalt(II) and Cobalt(III) complexes containing *N,N'*-ethylenebis(acetylacetonimine) dianion (baen) or *N,N'*-ethylenebis(salicylideneimine) dianion (salen) have been known for some time.[1–15] All the reported

---

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

[2] P. Pfeiffer, E. Breith, E. Lübbe, and T. Tsumaki, *Ann. Chem.*, **503**, 84 (1933).

[3] K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955); **60**, 1270 (1956).

[4] P. J. McCarthy, R. I. Hovey, K. Ueno, and A. E. Martell, *J. Amer. Chem. Soc.*, **77**, 5820 (1955).

[5] S. Yamada, H. Nishikawa, and E. Yoshida, *Proc. Japan Acad.*, **40**, 211 (1964).

[6] S. Yamada, *Coord. Chem. Rev.*, **1**, 415 (1966).

[7] H. Nishikawa and S. Yamada, This Bulletin, **37**, 8 (1964).

[8] G. W. Everett, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 2442 (1966).

[9] G. Costa, G. Mestroni, and L. Stefani, *J. Organometal. Chem.*, **7**, 473 (1967); G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *ibid.*, **6**, 181 (1966); G. Costa and G. Mestroni, *ibid.*, **11**, 325, 333 (1968).

[10] G. Costa and G. Mestroni, *Tetrahedron Lett.*, 1783 (1967).

[11] G. Costa, G. Mestroni, and G. Pellizer, *J. Organometal. Chem.*, **15**, 187 (1968).

[12] G. Costa, A. Puxeddu, and G. Tauzher, *Inorg. Nucl. Chem. Lett.*, **4**, 319 (1968).

[13] H. Yoneda and Y. Morimoto, This Bulletin, **41**, 2544 (1968).

[14] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970); B. M. Hoffman, D. L. Diemente, and F. Basolo, *ibid.*, **92**, 61 (1970).

[15] A. L. Crumbliss and F. Basolo, *Irong. Chem.*, **10**, 1676 (1971).

complexes have a planar configuration except for the complexes described in Reference 1). In a previous paper,[16] we reported the preparation and the halogenation reaction of the [Co(baen)(acac)] complex, and we mentioned that we could obtain only a *cis-β*-form complex, not a *cis-α* one. In this paper, we will report the preparation and the determination of the structures of two series of *cis-β* and *trans-planar*-forms cobalt(III)-baen, -salen complexes, and will describe the reason for isolating only *cis-β*-form complexes in the reactions of [Co(X)$(H_2O)_2$] (where X=baen or salen) and the bidentate ligands.

Experimental

Preparation of Complexes. *1)* trans-N,N′-*ethylenebis(acetylacetoniminato)diamminecobalt(III) perchlorate Dihydrate,* trans-[*Co(baen)*$(NH_3)_2$]$ClO_4 \cdot 2H_2O$ *(I)*: Five milliliters of 18 N ammonia were added to *trans-N,N′*-ethylenebis(acetylacetoniminato)diaquocobalt(II)[1] (3.2 g, 0.01 mol) in 200 m*l* of methanol, and then, to the resultant solution, a hydrogen peroxide solution was added. When sodium perchlorate monohydrate (5 g) in methanol was added to the above solution, yellowish-brown crystals were separated out. They were subsequently recrystallized from methanol. Yield, about 90%.

2) trans - N,N′ - *ethylenebis (acetylacetoniminato) dimethylaminecobalt(III) perchlorate Dihydrate,* trans-[*Co(baen)*$(CH_3NH_2)_2$]$ClO_4 \cdot 2H_2O$ *(II)*: This complex was prepared by using the method employed for the preparation of Complex I. Brown crystals were obtained in about a 90% yield.

3) trans - N,N′ - *ethylenebis(acetylacetoniminato)dipyridinecobalt(III) perchlorate,* trans-[*Co(baen)(py)*$_2$]ClO_4 *(III)*: This complex was also prepared by using the method employed for the preparation of Complex I. Brown crystals were obtained in about a 90% yield.

4) trans - N,N - *ethylenebis (acetylacetoniminato) dianilinecobalt(III) perchlorate,* trans-[*Co(bean)(aniline)*$_2$]ClO_4 *(IV)*: This complex was also prepared by the method used for Complex I. Brown crystals were obtained in about an 80% yield.

5) Sodium trans-*dinitro*-N,N′-*ethylenebis(acetylacetoniminato)-cobalt(III),* trans-*Na*[*Co(baen)*$(NO_2)_2$] *(V)*: *N,N′*-ethylenebis(acetylacetoniminato)diaquocobalt(II) (6.3 g, 0.02 mol) was dissolved in 200 m*l* of methanol, and then sodium nitrite (4 g, 0.06 mol) in 50 m*l* of water was added to this solution. The resulting solution was heated on a water bath and was concentrated to about 150 m*l* by evaporating the solvent. When the solution was cooled to 0°C, brown crystals were separated out. They were recrystallized from methanol. Yield, about 70%. From the IR spectrum, the coordination of the nitro groups was confirmed.

6) trans-*nitro* - N,N′ - *ethylenebis(acetylacetoniminato)aquocobalt(III),* trans-[*Co(baen)*$(NO_2)(H_2O)$] *(VI)*: Complex V was dissolved in water, and the solution was heated on a water bath for one hour. When the resulting solution was cooled to 0°C, dark green crystals were separated out. They were subsequently recrystallized from methanol. Yield, about 30%. From the IR spectrum, the coordination of the nitro group was confirmed.

7) trans - *nitro* - N,N′ - *ethylenebis(acetylacetoniminato)pyridinecobalt(III),* trans-[*Co(baen)*(NO_2)*(py)*] *(VII)*: Complex VI was dissolved in methanol, and then an equimolar amount of pyridine was added to the solution. When the resultant solution was slowly concentrated at room temperature, reddish-brown crystals were separated out. They were washed with methanol. Yield, about 60%.

8) cis - *β* - N,N′ - *ethylenebis(acetylacetoniminato)acetylacetonatocobalt(III),* cis-*β*-[*Co(baen)(acac)*] *(VIII)*: This complex was prepared by means of the known method given in Ref.16). Green crystals were obtained in about an 80% yield.

9) cis - *β* - N,N′-*ethylenebis(acetylacetoniminato)benzoylacetonatocobalt(III),* cis-*β*-[*Co(baen)(bzac)*] *(IX)*: Benzoylacetone (1.8 g, 0.011 mol) in 100 m*l* of methanol neutralized by potassium hydroxide (0.6 g, 0.011 mol) was added to a methanol (200 m*l*) solution of *N,N′*-ethylenebis(acetylacetonimonato)-diaquocobalt(II) (3.2 g, 0.01 mol). After air had been sucked through the solution for two hours, it was concentrated to about 100 m*l* by evaporating the solvent under reduced pressure. When the solution was then allowed to stand for two or three days, green crystals were separated out. They were recrystallized from methanol. Yield, about 70%.

10) cis-*β*-N,N′-*ethylenebis(acetylacetoniminato)-8-oxyquinolinatocobalt(III),* cis-*β*-[*Co(baen)(oxin)*] *(X)*: This complex was prepared by the method employed for the preparation of Complex IX, but using 8-hydroxyquinoline in place of benzoylacetone. Green crystals were obtained in a 40% yield.

11) cis - *β* - N,N′-*ethylenebis(acetylacetoniminato)ethylenediaminecobalt(III) Perchlorate Dihydrate,* cis-*β*-[*Co(baen)(en)*]$ClO_4 \cdot 2H_2O$ *(XI)*. An equimolar amount of ethylenediamine was added to a methanol solution of *N,N′*-ethylenebis(acetylacetoniminato)diaquocobalt(II). Then, to the resultant solution hydrogen peroxide solution was added. When sodium perchlorate monohydrate in methanol was added to the above solution, brown power was separated out. This was washed thoroughly with methanol. Yield, about 90%.

12) cis - *β* - N,N′-*ethylenebis(acetylacetoniminato)-1,10-dipyridylcobalt(III) Perchlorate,* cis-*β*-[*Co(baen)(dip)*]ClO_4 *(XII)*: This complex was prepared by using the method employed for complex XI. Recrystallized from methanol, green crystals were obtained in about an 80% yield.

13) cis-*β*-N,N′-*ethylenebis(acetylacetoniminato)-1,10-phenanthrolinecobalt(III) Perchlorate,* cis-*β*-[*Co(baen)(phen)*]ClO_4 *(XIII)*: This complex was prepared by the method employed for the preparation of Complex XII. Green crystals were obtained in about an 80% yield.

14) cis - *β* - N,N′ - *ethylenebis (salicylideneiminato) acetylacetonatocobalt(III),* cis-*β*-[*Co(salen)(acac)*] *(XIV)*: *N,N′*-ethylenebis(salicylideneiminato)cobalt(II)[2] (1.5 g) was dissolved in 200 m*l* of methanol, and potassium acetylacetonate was added to the solution. The resulting solution was heated on a water bath for fifteen minutes. When the resulting solution was concentrated to about 50 m*l*, yellowish-green crystals were separated out. They were subsequently recrystallized from methanol. Yield, about 90%.

15) cis-*β*-N,N′-*ethylenebis (salicylideneiminato) benzoylacetonatocobalt(III),* cis-*β*-[*Co(salen)(bzac)*] *(XV)*: This complex was prepared by using the method employed for Complex XIV. Yellowish-green crystals were obtained in about a 90% yield.

16) cis - *β* - N,N′-*ethylenebis (salicylideneiminato)ethylenediaminecobalt(III) Perchlorate Dihydrate,* cis-*β*-[*Co(salen)(en)*]$ClO_4 \cdot 2H_2O$ *(XVI)*: This complex was prepared by using the method used for Complex XI. A brown powder was obtained in an 80% yield.

17) cis - *β* - N,N′- *ethylenebis(salicylideneiminato)-1,10-dipyridylcobalt(III) Perchlorate,* cis-*β*-[*Co(salen)(dip)*]ClO_4 *(XVII)*: This complex was prepared by using the method employed for the preparation of Complex XII. Green crystals were obtained in about an 80% yield.

18) cis-*β*-N,N′-*ethylenebis(salicylideneiminato)-1,10-phenanthrolinecobalt(III) Perchlorate,* cis-*β*-[*Co(salen)(phen)*]ClO_4 *(XVIII)*. This complex was prepared by using the method employed for Complex XIII. Green crystals were obtained in about

---

16) Y. Fijii, This Bulletin, **43**, 1722 (1970).

Table 1. Elemental analyses data of the complexes

Complex		C (%)	H (%)	N (%)
		Found (Calcd)	Found (Calcd)	Found (Calcd)
$[Co(bean)(NH_3)_2]ClO_4 \cdot 2H_2O$	(I)	31.76 (31.97)	6.36 (6.27)	12.43 (12.43)
$[Co(bean)(CH_3NH_2)_2]ClO_4 \cdot 2H_2O$	(II)	35.25 (35.11)	6.65 (6.75)	11.82 (11.70)
$[Co(bean)(py)_2]ClO_4$	(III)	49.15 (49.02)	5.32 (5.25)	10.33 (10.40)
$[Co(bean)(aniline)_2]ClO_4$	(IV)	50.98 (51.02)	5.66 (5.72)	9.83 (9.92)
$Na[Co(bean)(NO_2)_2]$	(V)	36.41 (36.37)	4.55 (4.58)	14.01 (14.14)
$[Co(bean)(NO_2)(H_2O)]$	(VI)	41.72 (41.74)	6.13 (5.85)	12.19 (12.17)
$[Co(bean)(NO_2)(py)]$	(VII)	50.27 (50.24)	6.01 (5.71)	13.94 (13.79)
[Co(bean)(acac)]	(VIII)	53.68 (53.55)	6.80 (6.63)	7.36 (7.35)
[Co(bean)(bzac)]	(IX)	59.58 (59.72)	6.23 (6.16)	6.19 (6.33)
Co(bean)(oxin)]	(X)	59.31 (59.29)	5.53 (5.69)	9.76 (9.88)
$[Co(bean)(en)]ClO_4 \cdot 2H_2O$	(XI)	35.14 (35.26)	6.60 (6.36)	12.00 (11.75)
$[Co(bean)(dip)]ClO_4$	(XII)	49.12 (49.22)	4.68 (4.89)	10.52 (10.43)
$[Co(bean)(phen)]ClO_4$	(XIII)	51.33 (51.39)	4.69 (4.68)	9.99 (9.98)
[Co(salen)(acac)]	(XIV)	59.21 (59.43)	6.56 (6.60)	4.74 (5.00)
[Co(salen)(bzac)]	(XV)	63.64 (63.93)	5.58 (5.73)	4.88 (4.76)
$[Co(salen)(en)]ClO_4 \cdot 2H_2O$	(XVI)	41.39 (41.35)	5.54 (5.80)	11.02 (10.72)
$[Co(salen)(dip)]ClO_4$	(XVII)	53.48 (53.57)	3.61 (3.81)	9.58 (9.61)
$[Co(salen)(phen)]ClO_4$	(XVIII)	54.53 (54.51)	3.42 (3.60)	9.20 (9.08)

Table 2. NMR spectral data of *trans* form complexes

Complex	Solvent	Peaks of baen δ (ppm)				Peaks of others δ (ppm)
		C=CH	CH_2-CH_2	CH_3		
				(C=O)	(C=N)	
$[Co(bean)(NH_3)_2]ClO_4$	D_2O	5.13	3.61	2.25	2.08	
	d-DMSO	4.94	3.47	2.12	1.98	
$[Co(bean)(CH_3NH_2)_2]ClO_4$	D_2O	5.13	3.62	2.25	2.08	1.55 (CH_3NH_2)
	d-DMSO	4.93	3.47	2.13	2.00	1.50, 1.40, 1.30 (Triplet of CH_3NH_2)
$[Co(bean)(py)_2]ClO_4$	D_2O	5.02	3.73	2.26	2.04	7.2—8.2 (Multiplet of py)
$[Co(bean)(aniline)_2]ClO_4$	*d*-DMSO	4.93	3.60	2.18	2.08	6.6—7.2 (Multiplet of aniline)
$Na[Co(bean))NO_2)_2]$	D_2O	5.32	3.63	2.22	2.11	
$[Co(bean)(NO_2)(H_2O)]$	*d*-DMSO	4.97	3.61	2.16	2.05	
$[Co(bean)(NO_2)(py)]$	*d*-DMSO	4.95	3.62	2.15	1.99	7.2—8.2 (Multiplet of py)
$[Co(salen)(NH_3)_2]ClO_4$	*d*-DMSO	8.15	(CH=N of salen)	ca. 3.7	(CH_2-CH_2)	6.5—7.5 (Multiplet of phenyl group)
$[Co(salen)(CH_3NH_2)_2]ClO_4$	*d*-DMSO	8.22	(CH=N of salen)	ca. 3.7	(CH_2-CH_2)	6.5—7.5 (Multiplet of phenyl group) 1.50, 1.40, 1.30 (Triplet of CH_3NH_2)

an 80% yield.

The elemental analyses data of all the complexes are summarized in Table 1.

Measurements. The NMR spectra of the complexes were recorded with a Hitachi R-20 spectrometer (60 MHz) at 35°C, using D_2O, $CDCl_3$, or deuterated dimethylsulfoxide as the solvent. In all the NMR measurements, TMS or NaTMS was used as the internal reference.

Results anb Discussion

NMR Spectra of Complexes I, II, III, IV, V, VI, and VII. The NMR spectra of the *trans* complexes are summarized in Table 2, together with those of *trans*-form Co(III)-salen complexes. Some typical NMR spectra of *trans*-form complexes are shown in Fig. 1.

Complexes I, II, III, IV, V, VI, and VII, all of which involve unidentate ligands, show NMR spectra having one C=CH and two CH_3 signals with relative intensities of 1 : 3 : 3. Generally, three geometrical isomers, *trans-planar*, *cis-α*, and *cis-β*, are possible for these complexes.1) Complexes VI and VII, in which two unidentate ligands are present, show the typical NMR spectral pattern corresponding to the *trans* isomer. Therefore, these complexes, VI and VII, can be assigned a *trans*-form structure. Considering that the well-known oxygen carriers, Co(II)-baen complexes,3,8–10,14) also have a *trans*-form structure, all the complexes, I, II, III, IV, V, VI, and VII, can be concluded to have *trans-planar* structures.

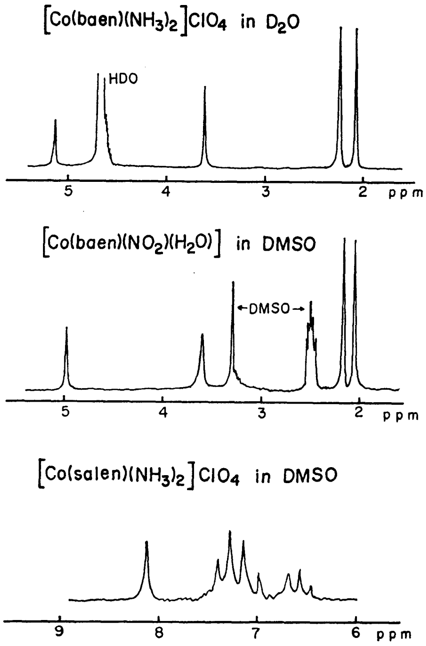


Fig. 1. Typical NMR spectra of *trans* form Co(III)-baen, -salen complexes.

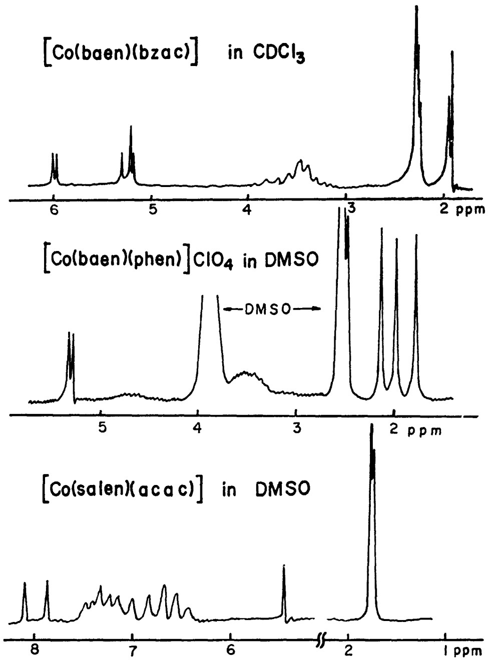


Fig. 2. Typical NMR spectra of *cis-β* form Co(III)-baen, -salen complexes.

The Co(III)-salen complexes containing ammonia or methylamine, which were prepared by using the well-known method described in Ref. 5), show NMR spectra with one CH=N signal; it is confirmed form study of their NMR spectra that these Co(III)-salen complexes take the *trans-planar* structure.

NMR Spectra of Complexes VIII, IX, X, XI, XII, and XIII. The data of the NMR spectra of *cis-β*-form Co(III)-bean, -salen complexes are listed in Tables 3 and 4, while some typical NMR spectra of these complexes are also shown in Fig. 2.

The baen complexes VIII, X, XI, XII, and XIII, show NMR spectra with two C=CH and four CH$_3$ signals for baen (the relative intensities of their peaks are 1 : 1 : 3 : 3 : 3 : 3). Since these spectral patterns correspond to the structure of the *cis-β*-form, as has been mentioned in a previous paper,[16] Complexes VIII, X, XI, XII, and XIII are assigned *cis-β*-form structures. On the other hand, Complex IX shows three C=CH signals with relative intensities of 1 : 2 : 1 for baen, two C=CH signals with relative intensities of 1 : 1 for bzac, and six CH$_3$ signals with relative intensities of 9 : 6 : 3 : 3 : 3 : 6 for baen and bzac. Although all the signals are not clearly resolved in this NMR spectrum, it can easily be understood that Complex IX does not contain only one species of the three

Table 3. NMR spectral data oe *cis-β* form cobalt(III)-baen complexes

Complex	Solvent	Peaks of baen (ppm)				Peaks of others (ppm)
		C=CH	CH$_2$-CH$_2$	CH$_3$		
				(C=O)	(C=N)	
VIII	CDCl$_3$	5.21(1) 5.19(1)	*ca.* 3.4*	2.25(6)	2.32(3) 1.98(3)	5.36(1) (C=CH of acac) 2.11(3), 1.75(3) (CH$_3$ of acac)
IX	CDCl$_3$	5.29(1) 5.21(2) 5.18(1)	*ca.* 3.4*	2.29(9), 2.25(6), 2.23(3), 2.20(3), 1.95(3), 1.91(6)		(two of them are CH$_3$ of bzac) 6.00(1), 5.97(1) (C=CH of bzac)
X	CDCl$_3$	5.25(1) 5.03(1)	*ca.* 3.5*	2.37(3) 2.13(3)	2.05(6)	6.8—8.2 (multiplet of oxin)
XI	*d*-DMSO	5.19(1) 5.04(1)	*ca.* 3.5*	2.18(3) 2.16(3)	2.00(3) 1.71(3)	
XII	*d*-DMSO	5.27(1) 5.24(1)	*ca.* 3.5*	2.40(3) 2.06(3)	2.01(3) 1.87(3)	7.5—8.8 (multiplet of dip)
XIII	*d*-DMSO	5.31(1) 5.26(1)	*ca.* 3.5*	2.45(3) 2.11(3)	1.96(3) 1.75(3)	7.9—9.0 (multiplet of phen)

( ) represents No. of H's. * shows the complicated band.

TABLE 4. NMR SPECTRA OF *cis-β* FORM COBALT(III)-SALEN COMPLEXES

Complex	Solvent	Peaks of salen δ (ppm)		Peaks of others δ (ppm)
		CH=N	CH_2-CH_2	
XIV	*d*-DMSO	8.07(1) 7.87(1)	*ca.* 3.8[a](4)	5.43(1) (C=CH of acac)
				1.74(3) 1.72(3) } (CH_3 of acac)
XV	*d*-DMSO	8.15(1) 7.88(1)	*ca.* 4.1[a](4)	6.13(1) (C=CH of bzac)
				1.89(3) (CH_3 of bzac)

( ) represents No. of H's.

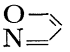
a) The complicated band.

possible geometrical isomers—*cis*-α, *cis*-β_1, and *cis*-β_2, but that it is either a 1 : 1 mixture of two *cis-β* isomers or a 1 : 1 mixture of *cis*-α and one of the two *cis-β* isomers. However, as the NMR spectra expected for the two cases are thought to be nearly identical with each other, we can not distinguish whether the observed NMR spectrum corresponds to the former case or to the latter one. Since Complexes VIII, X, XI, XII, and XIII take only the *cis-β*-form structure, as has been mentioned above, and since all the above Co(III)-baen complexes are synthesized by using nearly the same reaction conditions, Complex IX is also thought to have the *cis-β*-form structure. Thus, Complex IX can be assummed to be a 1 : 1 mixture of two *cis-β* isomers.

Despite the fact that Complex IX contains two *cis-β*-form isomers in a relative ratio of 1:1, Complex X contains only one *cis-β*-form isomer, though two *cis-β* isomers are also possible in this case. As will be mentioned later, this can be mainly ascribed to the steric nature of these complexes.

NMR Spectra of Complexes XIV, XV, XVI, XVII, and XVIII. Complexes XIV and XV show two CH=N signals and one C=CH signal. Therefore, we can safely assign the *cis-β* structure to these complexes. However, in the cases of Complexes XVII and XVIII, the CH=N signal overlaps with the signals of the coordinated dipyridyl or phenanthroline. Therefore, it is difficult to determine the structure of these complexes from the NMR spectra only. Also it is difficult to determine the structure of Complex XVI because of its low solubility in a solvent. However, since the baen complexes containing bidentate ligands have *cis-β*-form structures, and since the salen complexes of acac and bzac have also *cis-β*-form structures, we can assign a *cis-β*-form structure to Complexes XVI, XVII, and XVIII, too. The reason for isolating only one *cis-β*-form isomer in Complex XV can be ascribed to the steric interaction of this complex, which will be discussed later.

The Preference of the trans-*Planar Structure in* [*Co*(*baen*)(*A*)$_2$]*ClO*$_4$ *and the Preference of a* cis-*β Structure in* [*Co*(*baen*)(*Y*)]*ClO*$_4$. In the reaction between *trans*-[Co(baen)(H_2O)$_2$] and the monodentate ligands, we can obtain only the *trans*-planer-form complexes in high yields. On the other hand, in the reaction between *trans*-[Co(baen)(H_2O)$_2$] and the bidentate ligands, we can obtain only *cis-β*-form complexes in high yields. In both cases, as we used the *trans*-[Co(baen)(H_2O)$_2$] as the starting material, it is thought possible that the configuration of the reaction products depends strongly on the reaction mechanism. In order to confirm this point, we prepared the complexes starting from the coblat(II) ion. The complex which was prepared by mixing the cobalt(II) ion, ammonia, and baen (in this order) gives the same NMR spectrum as that of Complex I. The complex which was prepared by mixing the cobalt(II) ion, phenanthroline, and baen (in this order) gives a NMR spectrum corresponding to the *cis-β*-form structure. From these observations, it can be concluded that the formation of the *trans*-form complex in the case of the unidentate ligands and the formation of only the *cis-β*-form complex in the case of the bidentate ligands do not depend on only the reaction mechanism.

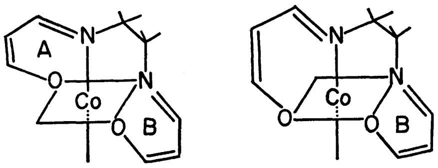
Relative Stability of the Configuration. It has been established that baenH_2 takes the ketamine structure in solution.[17] On the other hand, although two resonance structures, ketamine and ketimine, are possible, the coordinated baen is thought to take the ketimine structure exclusively.[4] In the cases of the coordinated salen, it is clear that the salen takes the ketimine structure, because free salenH_2 takes the ketimine structure and the resonance from ketimine to ketamine structures in salen complexes is almost impossible because of the phenyl group.[3,18] Therefore, it can be thought that the C=N bonds of the coordinated baen and salen have mainly a double-bond character; therefore, their nitrogen atoms take the electronic configuration of the sp^2 hybridization. From the above structual restrictions, and the fact that the  group of baen and salen is planar in nature, it is expected that the coordinated baen and salen will prefer the planar to all other configurations, corresponding to the *trans*-planar structure of octahedral complexes. The reason why only *trans*-form complexes isolated in the reaction between *trans*-[Co(baen)-(H_2O)$_2$] and the unidentate ligands is thought to be mainly based on the above facts.

In the cases of the baen and salen complexes which contain a bidentate ligand, baen and salen can not take a *trans*-planar configuration, but only a *cis*-α or *cis-β* form. When baen and salen take a *cia*-α

---

[17] G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 2099 (1961).

[18] G. N. Weinstein, M, J. O'Connor and R. H. Holm. *Inorg. Chem.*, **9**, 2104 (1970).



cis-α *cis*-β

Fig. 3. The geometrical structures of *cis*-α and *cis*-β forms Co(III)-baen, -salen backbones.

or *cis*-β-form, it can be concluded form the molecular model test that the chelate rings A, B and B in Fig. 3 are distorted from the plane of $\mathrm{Co}\langle{}^{\mathrm{O}}_{\mathrm{N}}$ by about 30°. This distortion will cause the decrease in the π-bond-formation ability of baen and salen with the cobalt(III) ion as compared with that in the *trans*-planar complexes. From this point of view, it is concluded that the relative stabilities among three configurations are as follows: planar>*cis*-β>*cis*-α.

In the cases of the *cis*-β-form complexes, some steric interaction between the coordinated baen, salen, and the bidentate ligands is observed in their molecular model tests. Since the chelate ring B is distorted from the plane of $\mathrm{Co}\langle{}^{\mathrm{O}}_{\mathrm{N}}$ by about 30°, as is shown in Fig. 3, when the sterically bulky groups such as benzoylacetone and 8-oxyquinoline are coordinated to the cobalt(III)-baen, salen backbone, some steric interaction between the bulky groups and the methyl, phenyl groups of the distorted $\genfrac{}{}{0pt}{}{\mathrm{O}-\rangle}{\mathrm{N}=\rangle}$ group occurs. This steric hindrance is thought to be much larger in salen than in baen, and much larger in 8-oxyquinoline than in benzoylacetone. This steric hindrance is thought to be the main reason why only one *cis*-β-form isomer is siolated in the cases of Complexes X and XV.

The authors wish to express their deep thanks to Dr. M. Kodama of Ibaraki University for his encouragement.